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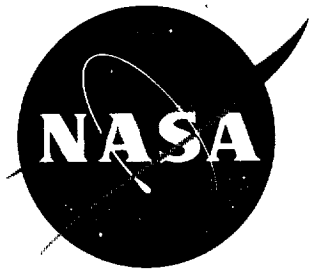

TECHNICAL NOTE
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THE PRODUCTION OF SUBMICRON METAL POWDERS BY BALL MILLING WITH GRINDING AIDS

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SUMMARY

Normally, ductile metal powders cannot readily be ground to submicron particle sizes because of agglomeration or welding phenomena which occur in the grinding mill. This paper describes how nickel and several other metal powders have been ground by ball milling to sizes as fine as 0.1 micron through the use of selected grinding aids. Various grinding aids (metal salts with different ion size, valence, and polarizability) plus conventional surfactants were employed. Ethyl alcohol, water, cyclohexane, n-heptane, and methylene chloride were used as grinding fluids. Milling was conducted with chromium, iron, copper, silver, and nickel powders of different particle sizes.

Generally salts proved more effective as grinding aids than surfactants. The effectiveness of a salt as a grinding aid was found to be related to the valence characteristics and complexity of its ions. All the metal powders just mentioned were successfully ground to sizes less than 1 micron. The type of grinding fluid employed significantly affected the grindability of the metal powders.

The time required to obtain submicron metal powders can be decreased by using the grinding aids in an attritor rather than a conventional ball mill. The method is economical and can also be applied to alloy powders and refractory compounds.

INTRODUCTION

Metal and alloy powders have many applications. They are used to produce reagents, pigments, coatings, solders, brazes, rocket propellants, and parts for industry by powder metallurgy techniques. Metal powders

[1]A shorter version of this report was presented at the Fall Meeting of the Metallurgical Society of the American Institute of Mining, Metallurgical, and Petroleum Engineers, Inc., Philadelphia, Oct. 17-20, 1960. The material was subsequently published in the Society's Transactions, vol. 221, no. 6, Dec. 1961, pp. 1105-1110. The present report is being released, by arrangement with the Society, to provide for further distribution and to make some additional details of the work generally available.

may also be combined with refractory compounds to produce cermets and dispersion-hardened products. Thus, fine and clean metal powders can be advantageously employed in many fields for research, development, and production.

One of the interests of the Lewis Research Center has been to explore the potentialities of the dispersion-strengthening process. References 1 to 4 present evidence that the strength of metal products may increase with decreasing interparticle spacing of the dispersed material. One method of achieving small interparticle spacing is to combine fine metal and refractory powders, preferably below 1 micron in size. However, until very recently the finest metal powders that could be obtained from commercial suppliers were 1.0 micron. Interest was therefore developed in providing finer metal powders for dispersion-hardening studies.

The production of fine metal powders may be approached by nucleation and growth processes, such as vapor condensation or precipitation from solution, or by mechanical comminution. Information obtained from the literature (refs. 5 and 6) and from prior experimental work performed by the NASA led to a consideration of ball milling as a technique for producing the desired materials. The method is economical and can also be applied to alloys and refractory compounds.

Some of the variables associated with ball milling are the size, material, and construction of the grinding container, the nature and amount of the grinding material and material to be ground, the nature and amount of the grinding liquid and grinding aid, if employed, and the grinding time. In all ball milling agglomeration due to welding or flocculation can occur as well as grinding. For given grinding conditions the ultimate particle size is limited to that obtained when equilibrium is reached between the rate of grinding and the rate of agglomeration. Because of these opposing tendencies, greater difficulty is often encountered in the grinding of ductile metals, which have a greater tendency to weld together than do brittle or friable metals (ref. 7). To help delay flocculation or welding, grinding aids are often used. For example, stearin is used in the ball milling of aluminum powder (refs. 8 to 10).

In current industrial practice a large number of surface-active agents variously termed surfactants, dispersants, or lubricants are employed as grinding aids. These products are generally composed of large organic molecules with polar and nonpolar groupings. Preliminary experiments by the NASA indicated that the use of various grinding aids with different grinding fluids could produce very large differences in grinding effectiveness. The experiments also showed that more polar compounds might serve as effective grinding aids for metals. Consequently, inorganic salts as well as conventional surfactants were tried as grinding aids for ball milling metal powders.

The principal objective of this investigation was to produce fine metal powders of an average particle size of less than 1 micron by ball milling the powders with selected grinding aids (surfactants and inorganic salts) and various grinding fluids. A secondary objective has been to attempt to explain the large variations observed in grinding behavior by postulating a number of grinding mechanisms and correlating various parameters with grinding effectiveness.

Three groups of ball-milling experiments were run, one in which the grinding aid was varied, a second in which the grinding fluid was varied, and a third in which the material being ground was varied. A total of 22 salts, 11 surfactants, 5 grinding fluids, and 11 metal powders (involving 5 different metals) were used in the investigation.

MATERIALS, APPARATUS, AND PROCEDURE

In general, specific amounts of different metal powders with various grinding liquids and grinding aids were ground with stainless steel balls in a milling jar for 2 to 15 days, and the grinding effectiveness was determined by measuring the particle sizes at various times. Most of the experiments consisted in varying the grinding aid employed and were performed using nickel powder (Inco carbonyl grade B), initially 2.5 microns, as the material being ground and 200-proof ethyl alcohol as the grinding fluid. (All metal powder sizes refer to average Fisher particle size.) In a second set of experiments grinding of the 2.5-micron nickel powder was tried in water, cyclohexane, n-heptane, and methylene chloride with four different salts and three surfactants. In a third group of experiments 200-proof ethyl alcohol was again used as the grinding fluid in the milling of chromium, iron, copper, silver, and nickel powders of various initial particle sizes.

Materials

The metal powders that were ground in this investigation are shown in table I. The source, type or grade, and Fisher particle size of the powders are listed in the table. Most of the experiments were conducted with the first item in the table, 2.5-micron Inco carbonyl grade B nickel powder. This powder was selected for the bulk of the experiments because it is relatively pure and fine and could be readily obtained in uniform large quantities. A number of duplicate runs were included in this series. In other experiments the same grinding techniques were applied to silver, iron, copper, chromium, and other nickel powders of different sizes, sources, and methods of manufacture.

Ethyl alcohol (200 proof) was selected as the grinding fluid for most runs because it was believed that polarity would tend to influence

the effectiveness of the grinding process, and alcohol has both polar and nonpolar characteristics. Additional experiments were run using a more polar liquid, distilled water, and also some less polar media, cyclohexane, n-heptane, and methylene chloride. Commercial grades of the grinding liquids were employed.

The salts used as grinding aids with their source and grade are listed in table II. Salts composed of ions of different size, valence, and polarizability were chosen for the investigation. The valences of the cations and anions are also listed in the table. Some of the salts were hydrated, while others were anhydrous. All the salts used were water soluble, which facilitated their removal from the metal powder when the grinding was completed.

The surfactants used as grinding aids are listed in table III. Because of the large number of surfactants available, an attempt was made to select representatives of series or general classes. The source and chemical name or formula are indicated where available.

Apparatus

The ball-mill jars used were $4\frac{3}{4}$ inches in diameter and 5 inches long and had a capacity of approximately 3 pints. They were constructed of an austenitic stainless steel and had three 1/4-inch-square cross-sectional ribs running the length of the jar at equal intervals around the inside circumference. The balls used were 1/2-inch diameter type 410 stainless steel ball bearings. The jars were rotated on a laboratory ball mill with a triple set of 4-foot rolls which could rotate 21 containers simultaneously. The slurries were filtered and washed on Buchner funnels.

A Fisher Sub-Sieve Sizer (which measures the resistance offered by the lightly packed powder to the flow of air under fixed pressure) was used to determine all reported average particle sizes (ref. 11). In a few cases where the results were below 0.2 micron or the porosity of the powder when compacted in the sample tube was greater than 0.8 (limit of the chart supplied by the manufacturer), the sizes were obtained by calculating the results directly from the formula supplied in the instruction manual. The results in this range were reproducible, and it is believed that the values are correct in order of relative size.

Procedure

All mill charges contained 300 milliliters of grinding liquid and 3000 grams of 1/2-inch stainless steel balls. When inorganic salts were used as the grinding aid, 70 grams of salt and 210 grams of metal powder

were employed, and with surfactants 6 grams of grinding aid and 300 grams of metal powder were used. The amounts used were based on general commercial practice and previous experiments. In most experiments with salts the amount used exceeded the solubility in the grinding fluid, and an excess of salt was present during the grinding operation. Sodium iodide, cesium chloride, and cerium nitrate were exceptions because of their very high solubility in ethyl alcohol.

The containers were loaded in groups of ten on the rolls and rotated at 48 rpm. After nominally 2, 4, 8, and 15 days of grinding, a sample weighing about 40 grams (powder plus liquid) was removed from each mill. If the suspension appeared too thick at the time of sample removal, grinding liquid was added until the slurry would just drip off the end of a spatula. (Preliminary experiments had indicated that neither sample removal nor viscosity of the slurry affected grinding effectiveness to any marked degree.)

Samples which contained inorganic salts were washed with hot tap water. After the grinding fluid was decanted, the beaker containing the ground powder was filled with water and stirred thoroughly, the powder was allowed to settle, and the liquid was poured off. Decantation with water was repeated ten times or more. In the case of the salts checked in table II, qualitative tests were used to determine when an ion of the salt was no longer present in the wash water. The powder in the beaker was then stirred with 190-proof ethyl alcohol, the suspension filtered through a Buchner funnel, and the filter cake dried in air at room temperature. The samples which contained surfactants were washed five times by decantation with 190-proof ethyl alcohol before the suspension was transferred to the filter funnel. Dried filter cakes were crushed and stirred for 30 to 60 seconds in an Osterizer in order to break up loose agglomerates that might have formed during the washing and drying. Then weighed amounts of powder were taken for particle-size determinations.

Chemical analyses were performed on a number of powders to determine the extent of oxidation and the extent of solvent or salt retention after washing.

RESULTS

Use of Salts as Grinding Aids

Table IV gives the results of experiments in which inorganic salts were used as grinding aids in ethyl alcohol to grind 2.5-micron Inco carbonyl grade B nickel powder. The salts are listed in order of grind-ind effectiveness, and particle sizes are listed for nominal grinding times of 2, 4, 8, and 15 days. In comparing the final particle sizes

(after 15 days of grinding) with the initial size, it can be noted that the standard (run 1) increased in size from 2.5 to 7.4 microns, and all the salts improved the grinding conditions over those of the standard. Of the 22 salts selected, 16 produced final particle sizes less than the original 2.5 microns, and of these 12 were less than 1.0 micron. The powders ground with 11 of the most effective salts were in the submicron range in 4 days. The smallest final particle size noted, 0.1 micron, was obtained with cerium nitrate ($Ce(NO_3)_3 \cdot 6H_2O$) and aluminum nitrate ($Al(NO_3)_3 \cdot 9H_2O$).

Reproducibility of Results

Table V shows the results of grinding experiments designed to determine the reliability of the grinding methods employed. Ten salts that produced varying degrees of grinding effectiveness were chosen for further study. In most cases good reproducibility in final particle size was obtained. Reproducibility appears to be better in the finer particle size ranges (below 1.0 micron). The major discrepancy in final particle size obtained results from the duplicate run with lithium chloride (run 27).

Surfactants Used as Grinding Aids

The ball-milling results obtained using surfactants as grinding aids are given in table VI. One run with cetyl alcohol (run 35) gave a final particle size greater than the standard (8.2 microns). Of 11 products investigated, 9 produced nickel powders with particle sizes greater than the original size, and 2 gave smaller sizes. Both of these runs, 44 and 45 with oleic and stearic acids, resulted in final average particle sizes of less than 1 micron.

Effect of Grinding Liquids on Grinding Effectiveness

A marked effect, produced by the grinding fluid, on the grinding effectiveness obtained with a number of salts and surfactants is evident from the final average particle sizes listed in tables VII and VIII. With NaCl, Aerosol OT, and Armeen 18 grinding or agglomeration was obtained depending on which grinding fluid was used. Even when grinding was achieved with all five liquids, significant differences in final particle size were obtained by varying the grinding fluid. No consistent pattern of effective grinding combinations such as salts or surfactants with polar or nonpolar liquids can be noted in these results.

Application to Various Metal Powders

Table IX gives the results obtained from grinding iron, chromium, silver, copper, and a number of nickel powders of varying particle size with ethyl alcohol and potassium ferricyanide. The initial sizes, varying from 2.1 to 30.0 microns, were reduced in 15 days to average particle sizes ranging from 0.1 to 0.6 micron. The smallest particles produced, 0.1 micron, were obtained by grinding a 7.3-micron iron powder, and the largest final size, 0.6 micron, was obtained by grinding an 8.5-micron chromium powder. The largest powder tried, 30.0-micron copper, was reduced to a final average particle size of 0.4 micron. It is interesting to note that the largest final particle size, 0.6 micron, was obtained with a relatively brittle metal, chromium. Also, all the powders in this group except chromium were reduced in size to the submicron range within 5 days of grinding.

Grinding Curves

Figures 1 to 5 are plots of particle size against time for most of the data shown in tables IV to IX. It was found during the plotting that the graphs fall into the four generalized types illustrated in figure 6. The curves have been grouped roughly according to type and final particle size as follows:

Type I curves (fig. 1(a)) show a continuous increase in particle size throughout the run. The curves in figure 1(b), designated type I(b), generally agglomerate but show a small decrease in particle size for part of the run.

Type II curves (fig. 2) show a decrease in particle size followed by an increase.

Type III curves (fig. 3) show an increase in particle size followed by a decrease.

Type IV curves (figs. 4 and 5) show a continuous decrease in particle size.

Type I curves result from the use of the least effective grinding aids, type IV from the most effective, and types II and III from those of intermediate effectiveness (see table X). The graphs facilitate analysis and discussion of the results. While the results are based on 15 days of ball milling, it can be noted that most experiments with type IV grinding curves reached submicron sizes in less than 4 days of grinding.

Chemical Analyses of Ground Metal Powders

Chemical analyses for oxygen, carbon, nitrogen, and various salt ions are given for the original Inco grade B 2.5-micron nickel powder and for the powder after grinding with different grinding aids in table XI. A standard without grinding aids shows a pickup of 0.05 percent iron from the steel balls and container.

DISCUSSION OF RESULTS

Effect of Grinding Aids and Grinding Fluids

The results of the investigation show that submicron metal powders as small as 0.1 micron can be produced by ball milling by the use of suitable grinding aids and grinding liquids. In the most successful experiments submicron sizes were obtained in less than 4 days of grinding.

The experiments have demonstrated the very significant effect of the grinding aid on grinding effectiveness. This is readily observed from the fact that, by starting with a 2.5-micron nickel powder and varying the grinding aid employed, a variation in final particle size of more than 8 microns, from 0.1 to 8.2 (a factor of 80), was obtained after ball milling for 15 days.

The experiments have also demonstrated the marked effect of the grinding liquid on grinding effectiveness. This can be noted from the fact that a reduction or increase in size of the 2.5-micron nickel powder can be produced by varying the grinding fluid, and differences as great as 4.5 microns in final particle size were obtained.

The wide applicability of ball milling with grinding aids was demonstrated by experiments in which powders of five different metals of varying properties, sources, methods of manufacture, and initial particle sizes, ranging from 2.1 to 30.0 microns, were ground to final sizes of 0.1 to 0.6 micron in 15 days. The grinding time required to reach the submicron range was practically the same (about 4 days) for both the large and small powders.

In addition the data have clearly established the effectiveness of inorganic salts as grinding aids for metal powders. Out of 22 salts tried as grinding aids, 12 produced nickel powders with average particle sizes below 1 micron in 15 days, while only 2 of 11 surfactants produced submicron nickel powders when used as grinding aids under the same conditions. Also five salts helped to reduce the average particle size of the 2.5-micron nickel powder to less than 0.3 micron, which was the smallest size obtained with a surfactant.

Factors That May Influence Grinding

While the smallest particle size produced in this study was 0.1 micron, it is conceivable that by a consideration of the nature of the grinding action the lower limit could be extended below the present range. From a purely mechanical point of view it should be noted that at the end of 15 days of grinding the grinding curves of many of the successful experiments still had negative slopes. Therefore it appears that a decrease in particle size could be obtained by longer grinding. Subsequent experiments have shown that the time of grinding could be substantially reduced by using the grinding aids and liquids in an attritor ball mill, which achieves more efficient use of the balls by rotating them with a stirring arm instead of rolling them. With an attritor mill 1.0-micron powder was produced in 10 hours, and 0.1-micron powder in 72 hours. Thus milling time can be reduced from 5 to 10 times. Preliminary experiments have also shown that the grinding methods are also applicable to alloy powders and refractory compounds. Particle sizes of a number of the ground powders determined recently by the BET method are noted in the appendix.

Theoretical Discussion of Grinding Mechanisms

It has been noted earlier that in ball milling both grinding and agglomeration of particles occur simultaneously. Finer particle sizes may therefore be obtained by enhancing the grinding rate or retarding the rate of agglomeration.

The mechanisms by which a grinding aid may actively promote comminution may be broadly classified as mechanical, chemical, and physical. The mechanical factors operate directly on the particle through the impacting and shearing action of the balls and facilitate deformation and abrasion, particularly of soft, malleable, brittle, flat, lacey, or dendritic particles. The chemical and physical factors may operate by forming a surface film on the particles which can retard welding and flocculation and enhance deformation and abrasion. A number of these factors which could influence ball milling will be considered briefly, and then an attempt will be made to relate the mechanisms to the experimental data. While the data are not adequate to distinguish the relative importance of the two processes, it is believed that grinding aids are more active in retarding agglomeration than in facilitating fracture of the metal particles.

Possible Effects of the Grinding Aid on Mechanical Abrasion

Ball milling operates by the impacting of the balls on the powder. Some of the variables in this process include the size of the balls, the size and rate of rotation of the mill, and the shape and hardness of the

materials to be ground. Since salt crystals were present in most of the milling experiments, the crystal edges of the salt could conceivably assist the steel balls in abrading the metal powders. Data on salt hardness and particle size which are presented in the analysis section tend to discount the extent to which abrasive action contributes to the effective functioning of a grinding aid.

Possible Effects of Surface Films on Abrasion of Metal Powders

The metal powder may react with the surrounding air to form an oxide or with the salt or surfactant used as a grinding aid to form a surface compound. The surface film, if thick enough would have the flow and fracture characteristics of a salt, which generally would be more brittle than the metal. In addition to films formed by chemical reaction, adsorbed films of gases, liquids, ions, salts, or surfactants can result from unsaturated attractive forces on the surface of the particles. Surface films could aid grinding by modifying the properties of the underlying metal layers. The phenomenon of surface films affecting the properties of metals has been observed by Rehbinder and others (ref. 12). Rehbinder noted that surface-active films may influence the deformation, hardness, fatigue strength, strain hardening, brittle fracture, and surface energy of metals. In order to explain such effects occurring to a depth of 0.1 millimeter, he postulated the opening up of microcracks under lower stresses then are normally required. Some question has been raised in the literature as to the validity of these interpretations (ref. 13). Some question might also be raised as to whether effects such as those postulated by Rehbinder could be applicable to grinding mechanisms. Nevertheless it seems reasonable that very small particles with a high surface-to-volume ratio would be more susceptible to surface effects than bulk materials. Therefore surface films could conceivably affect the characteristics of the particles in a way that would assist grinding.

Possible Effects of Adsorbed Ion Films on Dispersion of Metal Powders

Adsorbed ions can also promote dispersion of the particles through the formation of similarly charged electrostatic layers on the surface of the ground particles, which then tend to repel one another. This phenomenon is analogous to the surface charges which lend stability to colloidal suspensions.

In colloids, the stability of a suspension is increased by increasing the concentration of similarly charged ions and decreased by adding ions of opposite charge (ref. 14). If a sufficient concentration of oppositely charged ions is added, the surface charge is neutralized, and at the point where the positive and negative charges approach equality

(the isoelectric point) the suspension becomes unstable and the particles agglomerate. An important consideration in colloid stability is the charge per unit area or the charge density. For example, it has been shown that multivalent ions are much more effective than monovalent ions in affecting the charge density and stabilizing colloids of like charge or agglomerating colloids of opposite charge (refs. 15 and 16). It is interesting to note that there are similarities between the behavior of colloidal suspensions and the grinding behavior of the various metal powders. This is not too surprising, since the powders ground in this investigation approach the colloidal size range.

If it is assumed in the grinding experiments that a minimum charge density is required on the surface of a metal particle for grinding to occur, the ion sorption mechanism can explain the grinding behavior as exemplified by the generalized grinding curves in figure 6. For experiments that give curves of type IV, which decrease continuously, the minimum surface charge required for grinding would be exceeded, and grinding would occur throughout the run. This is observed with effective aids. In experiments with type I grinding curves, which increase continuously, the minimum charge density required for grinding would not be exceeded at any point, and agglomeration would occur throughout the run. This is characteristic of ineffective aids.

With aids of intermediate effectiveness grinding or agglomeration may occur, depending on a number of factors such as the concentration of ions available, the amount of surface area exposed, and the adsorptive capacity of the surface (whether initial or fresh surface). If an insufficient number of ions is present or the ions are not adsorbed because of the low adsorptive capacity of the surface present, the required minimum charge density for grinding would not be attained, and the particles would agglomerate as is observed in the type III curves. During agglomeration surface area decreases, ion concentration in the solution is increased because of desorption, and some fresh adsorptive surface is formed. At some point the remaining surface would adsorb sufficient ions to attain the required minimum charge density, and grinding would start.

If sufficient ions are initially present and grinding starts, the new fresh surface area formed with its high adsorptive capacity may increase rapidly enough to deplete the available ions in solution, and the charge density may fall below the required minimum. Grinding will then stop as observed in the type II curves. From the preceeding considerations one might expect the type II curves to level off at this point, since a small amount of agglomeration should decrease the surface area and increase the ion concentration. The reason for the continued agglomeration is in doubt, but it could be that the rate of dissolution of the salt crystals is small compared with the rate of formation of new surface.

ANALYSIS OF GRINDING RESULTS IN TERMS OF MECHANISMS CONSIDERED

Effect of Solubility on Grinding Effectiveness

From the discussion of grinding mechanisms one might suspect that the sorption and surface film formation processes would function better in the presence of a large concentration of ions. Therefore one might also expect to find a relation between solubility of the grinding aid in the grinding liquid and grinding effectiveness. Since these salts are all water soluble, they would supply the greatest number of ions in this medium. Nevertheless it can easily be noted from tables VIII and IX that water is not a particularly good medium for effective grinding.

The grinding results in 200-proof ethyl alcohol show that it is a good medium for some grinding aids and a poor one for others. In table XII data are presented which show the solubility of various salts in 200-proof ethyl alcohol and the final particle size of nickel obtained when using these salts as grinding aids in this medium. It can be noted that both good and poor results were obtained with both soluble and insoluble salts. The results thus show that there is no relation between grinding effectiveness and the solubility of the salts used as grinding aids in the grinding medium.

Another possible source of ions in the nonpolar media may be water contamination and consequent solution of the water-soluble salts. Water could be present as an impurity, picked up from the atmosphere or acquired from the water of crystallization of the hydrated salts. It can be seen from table IV that both good and poor grinding results were obtained in 200-proof ethyl alcohol with both hydrated and anhydrous salts. Thus the results show that water contamination of 200-proof ethyl alcohol does not influence its effectiveness as a grinding fluid.

The better grinding efficiency obtained in some nonpolar media with the water-soluble salts as grinding aids may be due to better conditions for ion adsorption despite low salt solubility. This may be explained partly by smaller adsorption of nonpolar than polar solvents on the surface of the metal powder, which permits greater ion adsorption. In addition a polar liquid may compete with the powder for the available ions by forming solvent-ion bonds. Therefore the ions required for the minimum charge density may be more easily adsorbed by the powder in less polar media, where uncombined ions (not solvated) have access to clean metal surfaces. Thus grinding mechanisms dependent on adsorption of ions are considered distinct possibilities with water-soluble salts in nonpolar media.

Correlation of Salt Hardness with Grinding Effectiveness

Values are given in the following table for the Mohs hardness of various salts and the final particle sizes of 2.5-micron nickel powder obtained after 15 days of grinding with these salts as grinding aids:

Salt	Mohs hardness	Final particle size, microns
NaCl	2.0 to 2.5	4.0
$CuSO_4 \cdot 5H_2O$	2.5	.9
NaF	3.5	.8
$Al_2(SO_4)_3 \cdot 18H_2O$	1.5 to 2.0	.5

Examination of the data shows no correlation between salt hardness and grinding efficiency. It should be noted that water-soluble inorganic compounds are relatively soft, with Mohs hardness values ranging from 1.0 to 3.5, while the Mohs hardness of nickel runs from 5 to 6. In addition, many experiments in which nickel powder was milled with a large excess of salt present showed an increase in particle size, while experiments in which the salt was completely in solution in the grinding liquid showed a decrease in size. These facts tend to discount the importance of mechanical abrasion by salt crystals as a grinding mechanism in these experiments.

Correlation of Ion Size and Valence with Grinding Effectiveness

To correlate the valence and size of the salt cations and anions with grinding efficiency, graphs of the final particle size of nickel powder obtained on grinding for 15 days with various salts were plotted against cation size, anion size, and ion valence in figures 7 to 9. No pronounced correlation between cation or anion size is apparent from the data and plots in figures 7 and 8. Additional data are necessary before a more decisive conclusion can be reached as to the presence or absence of a relation. While adsorption of smaller ions would tend to give higher charge densities, this effect may be overshadowed by other factors such as valence and specific interactions between the metal particles and the salt ions.

Figure 9 seems to show a tendency towards better grinding effectiveness in the groups of salts which have multivalent anions or cations. It is important to note that in table IV all the salts with multivalent anions or cations, in which the anion is a radical rather than a single atom, gave high grinding effectiveness. In fact, the nine most effective salts

fell into this category. The observation that all highly effective salts had a multivalent ion also tends to support the ion adsorption colloid analogy, since it has been shown (e.g., ref. 13) that the ability of an ion to stabilize a colloid increases exponentially with valence.

Chemical Analyses of Ground Metal Powders

Chemical analyses (table XI) were run on a number of the ground nickel powders in order to determine their cleanliness and to detect ion sorption or reaction products which could perhaps indicate the operation of one or more grinding mechanisms.

An increase in carbon content after grinding may represent retention of grinding fluid or a salt ion containing carbon such as ferricyanide or ferrocyanide. This can be noted from the analyses of runs 7, 18, 20, 25, and 82. The progressive increase in carbon and nitrogen retention with grinding time observed in run 82 with potassium ferrocyanide may be associated with increased ion sorption or compound formation with increased surface area. In general small retention is observed for sodium, potassium, barium, and chloride, which indicates, at most, weak adsorption of these ions.

While a surface oxide layer could conceivably assist grinding as noted previously, a good judgment cannot be made on the basis of the oxygen figures in table XI, since it is not possible to distinguish between the oxidation which occurred in the slurry during grinding and that which occurred in handling the dry powder prior to analysis. However, the data for runs 19, 20, 51, and 82, which show that nickel powders ground to about the same particle size (0.2 to 0.3 micron) have a wide variation in oxygen content (2.49 to 13.32 percent), appear to minimize the relation between oxide content and grinding effectiveness. When low oxygen content is desired, it is necessary to perform all grinding of powders to submicron sizes under an inert gas atmosphere and to conduct all subsequent processing operations without access to air. By using grinding aids to grind nickel powder to 0.1 micron in an attritor mill under an argon atmosphere, it was possible to maintain the oxygen content below 1.5 percent. The oxygen figure was then reduced to 0.01 percent by hydrogen cleaning. It is believed that even cleaner fine ball-milled metal powders can be achieved with improved handling and cleaning techniques.

SUMMARY OF RESULTS

This investigation, which was undertaken to produce submicron metal powders and to explain variations in grinding behavior, has yielded the following results:

1. Submicron metal powders, as small as 0.10 micron, were produced by ball milling by the use of suitable grinding aids and grinding liquids, which have a large influence on grinding effectiveness.

2. Inorganic salts were effective as grinding aids for metal powders and were found to be superior to conventional surfactants for this purpose.

3. The grinding method employed is widely applicable. This was demonstrated by ball milling powders of five different metals of varying properties and particle sizes (2.1 to 30.0 microns) to submicron sizes in less than 5 days.

4. Four widely different types of grinding behavior were indicated by the shapes of the curves obtained on plotting particle size against grinding time. These showed either a continuous increase in particle size, an increase in size followed by a decrease, a decrease followed by an increase, or a continuous decrease throughout the run.

5. No correlation was found between salt hardness and grinding effectiveness. This evidence tends to discount mechanical abrasion by salt crystals as a grinding mechanism.

6. No correlation was found between the solubility of the grinding aid in the grinding fluid and grinding effectiveness.

7. No pronounced correlation between ion size and grinding effectiveness was apparent from the data.

8. A correlation was found between ion valence, and complexity, and grinding effectiveness in ethyl alcohol. The nine most effective salts were found to have a multivalent ion and a complex anion.

9. A proposed ion sorption mechanism offers a possible explanation for some of the observed grinding behavior.

10. A substantial decrease in grinding time has been achieved by using the grinding aids in an attritor type rather than a conventional ball mill. The method is economical and can also be applied to alloy powders and refractory compounds.

Lewis Research Center
National Aeronautics and Space Administration
Cleveland, Ohio, May 23, 1961

APPENDIX - PARTICLE SIZE OF SOME GROUND NICKEL POWDERS BY THE BET METHOD

In view of the fact that a number of the powders ground in the investigation had reached particle sizes at the limit of application of the Fisher Sub-Sieve Sizer (0.2 micron), it was considered of value to check the sizes of some of these powders by another method. The BET results for a number of fine powders given in table XIII are three to nine times lower than the Fisher values in the range below 0.5 micron and show seven of the powders to be smaller than 0.1 micron. The characterization of the average particle size of fine powders depends to an extent on the method used, and the BET method is considered to be more applicable in these low ranges (ref. 20). Further discussion on the Fisher and BET methods is available in references 21 and 22.

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TABLE I. - METAL POWDERS USED IN GRINDING EXPERIMENTS

Metal	Source	Type or grade (a)	Initial Fisher particle size, microns
Nickel	International Nickel Co.	Carbonyl grade B	2.5
	Sherritt Gordon Mines Ltd.	Grade FF 100	2.1
	Sherritt Gordon Mines Ltd.	Grade FF 325	4.8
	C. A. Hardy Co.	-300 mesh	9.3
	Sherritt Gordon Mines Ltd.	Grade F 325	17.0
	National Radiator Co.	F89A-A2	23.0
Iron	A. D. MacKay Co.	Carbonyl	3.2
	City Chemical Co.	Carbonyl, reduced	7.3
Chromium	C. A. Hardy Co.	-325 mesh, electrolytic	8.5
Silver	Metals Disintegrating Co.	Lot 61A	24.0
Copper	Metals Disintegrating Co.	Lot 61A	30.0

[a]All grades better than 98 percent pure metal.

TABLE II. - SALTS USED AS GRINDING AIDS

Salt	Formula	Source	Grade	Valence		Wash water tested (a)
				Cation	Anion	
Potassium ferricyanide	$K_3Fe(CN)_6$	Fisher Scientific Co.	Certified	+1	-3	√
Potassium ferrocyanide	$K_4Fe(CN)_6 \cdot 3H_2O$			+1	-4	√
Aluminum sulfate	$Al_2(SO_4)_3 \cdot 18H_2O$			+3	-2	
Ammonium molybdate	$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$			+1	-6	
Sodium dichromate	$Na_2Cr_2O_7 \cdot 2H_2O$			+1	-2	√
Tin chloride	$SnCl_4$			+4	-1	√
Potassium iodide	KI			+1	-1	√
Lithium chloride	LiCl			+1	-1	√
Sodium bromide	NaBr	Fisher Scientific Co.	c.p.	+1	-1	√
Sodium fluoride	NaF	Fisher Scientific Co.	c.p.	+1	-1	
Cerium nitrate	$Ce(NO_3)_3 \cdot 6H_2O$	Fisher Scientific Co.	Purified	+3	-1	
Thorium chloride	$ThCl_4$	Fisher Scientific Co.	Purified	+4	-1	√
Sodium chloride	NaCl	Fisher Scientific Co.	U.S.P.	+1	-1	√
Sodium iodide	NaI	Fisher Scientific Co.	U.S.P.	+1	-1	√
Sodium pyrophosphate	$Na_4P_2O_7$	Fisher Scientific Co.	Technical	+1	-4	
Nickel chloride	$NiCl_2 \cdot 6H_2O$	Mallinckrodt Chem. Co.	Analytical reagent	+2	-1	√
Aluminum nitrate	$Al(NO_3)_3 \cdot 9H_2O$			+3	-1	
Barium chloride	$BaCl_2 \cdot 2H_2O$			+2	-1	√
Copper sulfate	$CuSO_4 \cdot 5H_2O$	Mallinckrodt Chem. Co.	N.F.	+2	-2	√
Potassium dihydrogen phosphate	KH_2PO_4	J. T. Baker Co.	c.p.	+1	-3	
Ammonium acetate	$NH_4C_2H_3O_2$	J. T. Baker Co.	c.p.	+1	-1	
Cesium chloride	CsCl	----------	----------	+1	-1	√

[a]Tested for completeness of removal of salt after grinding and washing.

TABLE III. - SURFACTANTS USED AS GRINDING AIDS

Surfactant	Source	Chemical name or formula
Stearic acid	Fisher Scientific Co.	$C_{17}H_{35}COOH$
Oleic acid	J. T. Baker Co.	$C_{17}H_{33}COOH$
Aerosol OT	American Cyanamid Co.	Dioctyl ester of sodium sulfosuccinic acid
Alkaterge A	Commercial Solvents Co.	----------
Armeen 18	Armour Chemical Co.	Octadecylamine
G-672	Atlas Powder Co.	Glycerol sorbitan laurate
G-2854	Atlas Powder Co.	Polyoxyethylene sorbitol tetraoleate
Cetyl alcohol	----------	$C_{16}H_{33}OH$
Nuosperse 657	Nuodex Products Co.	----------
Surfynol 102	Air Reduction Co.	Di-tert-acetylene glycol
Tenlo 70	Griffin Chemical Co.	----------

TABLE IV. - EFFECTIVENESS OF VARIOUS INORGANIC SALTS AS GRINDING AIDS

[Material milled, 2.5-micron nickel powder; grinding liquid, 200-proof ethyl alcohol.]

Run	Salt	Data in fig. -	Average particle size, microns			
			Sample 1, 46 to 50 hr	Sample 2, 94 to 100 hr	Sample 3, 190 to 195 hr	Sample 4, 356 to 370 hr
1	None (standard)	1(a)	3.8	5.4	6.0	7.4
2	KI	1(b)	3.4	2.1	4.1	4.9
3	NaBr	1(b)	3.2	4.6	5.7	4.8
4	NaI	1(b)	3.4	4.2	4.8	4.7
5	NaCl	2(c)	1.7	2.7	3.6	4.0
6	CsCl	3(b)	5.1	4.2	[a]2.9	2.8
7	$BaCl_2 \cdot 2H_2O$	3(b)	4.4	4.0	[a]3.0	2.6
8	$SnCl_4$	2(d)	2.4	2.0	2.3	2.3
9	$NH_4C_2H_3O_2$	2(d)	2.3	[b]2.8	[a]3.2	2.1
10	LiCl	3(b)	3.6	4.2	[a]2.9	1.8
11	$NiCl_2 \cdot 6H_2O$	2(d)	1.6	2.0	1.5	1.6
12	$CuSO_4 \cdot 5H_2O$	4(a)	2.2	[b]1.8	[a]1.2	.9
13	NaF	4(a)	1.3	1.0	[a]1.0	.8
14	$ThCl_4$	4(a)	1.4	1.0	[a].9	.8
15	$Al_2(SO_4)_3 \cdot 18H_2O$	4(c)	1.6	.6	.5	.5
16	KH_2PO_4	4(b)	1.3	.9	[a].7	.5
17	$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$	4(c)	1.2	.8	.4	.4
18	$Na_4P_2O_7$	4(d)	1.3	.9	[a].5	.3
19	$K_4Fe(CN)_6 \cdot 3H_2O$	4(e)	1.1	.7	[a].5	.3
20	$K_3Fe(CN)_6$	4(d)	1.4	1.0	[a].6	.2
21	$Na_2Cr_2O_7 \cdot 2H_2O$	4(f)	1.1	[b].4	[a].4	.2
22	$Al(NO_3)_3 \cdot 9H_2O$	4(f)	.5	.4	----	.1
23	$Ce(NO_3)_3 \cdot 6H_2O$	4(f)	1.0	.5	[a].1	.1

[a]Data obtained after 205 to 211 hr of grinding.

[b]Data obtained after 121 hr of grinding.

TABLE V. - REPRODUCIBILITY OF GRINDING DATA

[Material milled, 2.5-micron nickel powder; grinding liquid, 200-proof ethyl alcohol.]

Run	Salt (grinding aid)	Data in fig. -	Average particle size, microns			
			Sample 1, 46 to 50 hr	Sample 2, 93 to 100 hr	Sample 3, 190 to 195 hr	Sample 4, 356 to 370 hr
2	KI	1(b)	3.4	2.1	4.1	4.9
24	KI	1(b)	3.2	3.0	3.6	4.6
5	NaCl	2(c)	1.7	2.7	3.6	4.0
25	NaCl	2(c)	2.0	3.2	3.4	4.1
9	$NH_4C_2H_3O_2$	2(d)	2.3	[a]2.8	[b]3.1	2.1
26	$NH_4C_2H_3O_2$	3(a)	4.4	4.6	2.9	2.3
10	LiCl	3(b)	3.6	4.2	[b]2.9	1.8
27	LiCl	2(c)	1.8	2.1	2.4	2.5
11	$NiCl_2 \cdot 6H_2O$	2(d)	1.6	2.0	1.5	1.6
28	$NiCl_2 \cdot 6H_2O$	3(a)	4.3	3.6	2.5	1.3
16	KH_2PO_4	4(b)	1.3	0.9	[b]0.7	0.5
29	KH_2PO_4	4(b)	1.5	.9	.6	.5
17	$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$	4(c)	1.2	0.8	0.4	0.4
30	$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$	4(c)	1.2	.9	.6	.4
19	$K_4Fe(CN)_6 \cdot 3H_2O$	4(d)	1.1	0.7	[b]0.5	0.3
31	↓	↓	1.2	.7	.4	.3
32			1.1	.6	.4	.3
20	$K_3Fe(CN)_6$	4(d)	1.4	1.0	[b]0.6	0.2
33	$K_3Fe(CN)_6$	4(d)	1.3	.8	.4	.2
21	$Na_2Cr_2O_7 \cdot 2H_2O$	4(f)	1.1	[a]0.4	[b]0.4	0.2
34	$Na_2Cr_2O_7 \cdot 2H_2O$	4(f)	1.2	.8	.6	.3

[a]Data obtained after 121 hr of grinding.

[b]Data obtained after 205 to 211 hr of grinding.

TABLE VI. - EFFECTIVENESS OF VARIOUS SURFACTANTS AS GRINDING AIDS

[Material milled, 2.5-micron nickel powder; grinding liquid, 200-proof ethyl alcohol.]

Run	Surfactant	Data in fig. -	Average particle size, microns			
			Sample 1, 48 to 50 hr	Sample 2, 93 to 94 hr	Sample 3, 189 to 191 hr	Sample 4, 354 to 357 hr
35	Cetyl Alcohol	1(a)	4.4	[a]6.9	7.3	8.2
36	Aerosol OT	1(a)	3.3	[a]5.4	5.5	6.1
37	Surfynol 102	1(a)	3.2	[a]4.8	4.8	6.1
38	G-672	2(a)	1.4	[a]3.8	4.7	4.6
39	Armeen 18	2(a)	1.0	[a]1.4	2.6	3.9
40	Tenlo 70	2(a)	1.3	[a]1.2	2.1	3.8
41	G-2854	2(b)	1.3	[a]2.5	3.4	3.7
42	Nuosperse 657	2(b)	1.0	[a]1.8	2.7	3.7
43	Alkaterge A	2(a)	2.1	[a]3.6	3.3	2.8
44	Oleic acid	2(d)	1.2	.5	.4	.8
45	Stearic acid	4(d)	.8	.5	.5	.3

[a]Data obtained after 123.5 hr of grinding.

TABLE VII. - EFFECT OF VARIOUS GRINDING LIQUIDS ON GRINDING EFFECTIVENESS AFTER 2, 4, 8, AND 15 DAYS

[Material milled, 2.5-micron nickel powder.]

Run	Grinding aid	Grinding liquid	Data in fig. -	Average particle size, microns			
				Sample 1, 46 to 50 hr	Sample 2, 93 to 100 hr	Sample 3, 190 to 195 hr	Sample 4, 355 to 370 hr
5	NaCl	Ethyl alcohol	2(c)	1.7	2.7	3.6	4.0
46		Water	3(b)	2.7	2.9	3.3	2.3
47		Cyclohexane	4(a)	1.5	1.3	1.0	.7
48		n-heptane	----	---	----	----	[a]1.5
49		Methylene chloride	2(d)	1.3	0.8	0.5	.7
18	$Na_4P_2O_7$	Ethyl alcohol	4(d)	1.3	0.9	[b]0.5	0.3
50		Water	4(c)	3.3	2.4	2.3	1.4
51		Cyclohexane	----	---	----	----	[a].7
52		n-heptane	----	---	----	----	[a]2.2
53		Methylene chloride	4(d)	1.9	1.4	0.8	.2
22	$Al(NO_3)_3 \cdot 9H_2O$	Ethyl alcohol	4(f)	0.5	0.4	----	0.1
54		Cyclohexane	----	---	----	----	[a]1.4
55		Methylene chloride	4(b)	0.4	0.5	0.3	.3
36	Aerosol OT	Ethyl alcohol	1(a)	3.3	[c]5.4	5.5	6.1
56		Water	2(d)	1.8	1.8	1.5	1.6
57		Cyclohexane	----	---	----	----	[a]1.6
58		n-heptane	----	---	----	----	[a]1.4
59		Methylene chloride	----	---	----	----	[a]1.2
39	Armeen 18	Ethyl alcohol	1(b)	1.0	[c]1.4	2.6	[a]3.9
60		Water	4(a)	1.4	1.1	1.0	.9
61		Cyclohexane	----	---	----	----	[a].6
62		n-heptane	----	---	----	----	[a].5
63		Methylene chloride	----	---	----	----	[a]2.2
44	Oleic acid	Ethyl alcohol	2(d)	1.2	0.5	0.4	0.8
64		Water	----	---	----	----	[a]1.1
65		Cyclohexane	----	---	----	----	[a].9
66		n-heptane	2(d)	1.3	0.6	0.4	1.0
67		Methylene chloride	----	---	----	----	[a]1.5
45	Stearic acid	Ethyl alcohol	4(d)	0.8	0.5	0.5	0.3
68		Water	----	---	----	----	1.5
69		Cyclohexane	----	---	----	----	[a].8
70		n-heptane	4(d)	0.7	0.4	0.4	.3
71		Methylene chloride	----	---	----	----	[a]2.0

[a]Only final particle size taken.
[b]Data obtained after 205 hr of grinding.
[c]Data obtained after 123.5 hr of grinding.

TABLE VIII. - EFFECT OF VARIOUS GRINDING LIQUIDS ON GRINDING EFFECTIVENESS AFTER 15 DAYS

[Material milled, 2.5-micron nickel powder.]

Grinding aid	Average particle size, microns				
	Water	Ethyl alcohol (200 proof)	Cyclohexane	n-heptane	Methylene chloride
NaCl	2.3	4.0	0.7	1.5	0.7
$Na_4P_2O_7$	1.4	.3	.7	2.2	.2
$Al(NO_3)_3 \cdot 9H_2O$	---	.1	1.4	---	.3
Aerosol OT	1.6	6.1	1.6	1.5	1.2
Armeen 18	.9	3.9	.6	.5	2.2
Oleic acid	1.1	.8	.9	1.0	1.5
Stearic acid	1.5	.3	.8	.3	2.0

TABLE IX. - EFFECT OF $K_3Fe(CN)_6$ ON GRINDING OF VARIOUS METAL POWDERS

[Grinding liquid, 200-proof ethyl alcohol.]

Run	Source of metal powder	Metal powder	Original particle size, microns	Data in fig. -	Average particle size, microns			
					Sample 1, 48 to 49 hr	Sample 2, 94 to 96 hr	Sample 3, 192 to 193 hr	Sample 4, 357 to 370 hr
72	Plastic Metals Co.	Ni	23.0	7	1.3	0.6	0.3	0.2
73	Sherritt Gordon Mines Ltd.	↓	17.0	↓	2.6	1.0	.5	.3
74	C. A. Hardy Co.	↓	9.3	↓	1.7	.8	.4	.3
75	Sherritt Gordon Mines Ltd.	↓	4.8	↓	2.0	.8	.4	.4
20	International Nickel Co.	Ni (carbonyl B)	2.5	↓	1.4	1.0	[a].6	.2
76	Sherritt Gordon Mines Ltd.	Ni	2.1	↓	1.4	.6	.3	.2
77	Metals Disintegrating Co.	Cu	30.0	9	0.4	0.5	0.5	0.4
78	Metals Disintegrating Co.	Ag (spherical)	24.0	9	1.9	.6	.4	.4
79	C. A. Hardy Co.	Cr (electrolytic)	8.5	8	2.2	1.7	1.1	0.6
80	City Chemical Co.	Fe (carbonyl reduced)	7.3	↓	6.4	1.0	.3	.1
81	A. D. MacKay Co.	Fe (carbonyl)	3.2	↓	1.1	.8	.5	.4

[a]Data obtained after 205.5 hr of grinding.

TABLE X. - CLASSIFICATION OF GRINDING AIDS BY SHAPE OF GRINDING CURVES

[Material milled, 2.5-micron nickel powder; grinding liquid, 200-proof ethyl alcohol, unless noted.]

Type I curves		Type II curves		Type III curves		Type IV curves	
Grinding aid	Particle size, microns	Grinding aid	Particle size, microns	Grinding aid	Particle size, microns	Grinding aid	Particle size, microns
Cetyl alcohol	8.2	Atlas G672	4.6	CsCl	2.8	$CuSO_4 \cdot 5H_2O$	0.9
Standard	7.4	[a]NaCl	4.1	$BaCl_2 \cdot 2H_2O$	2.6	Armeen 18 (H_2O)	.9
Aerosol OT	6.1	NaCl	4.0	[a]$NH_4C_2H_3O_2$	2.3	NaF	.8
Surfynol 102	6.1	Armeen 18	3.9	$NaCl(H_2O)$	2.3	$ThCl_4$	.8
KI	4.9	Tenlo 70	3.8	LiCl	1.8	NaCl (cyclohexane)	.7
NaBr	4.8	Atlas G2854	3.7	$Na_4P_2O_7(H_2O)$	1.4	$Al_2(SO_4)_3 \cdot 18H_2O$	.5
NaI	4.7	Nuosperse	3.7	[a]$NiCl \cdot 6H_2O$	1.3	KH_2PO_4	.5
[a]KI	4.6	Alkaterge A	2.8			$(NH_4)_2Mo_7O_{24} \cdot 4H_2O$	.4
		[a]LiCl	2.5			$Al(NO_3)_3 9H_2O$ (Meth Cl)	.3
		$SnCl_4$	2.3			$Na_4P_2O_7$	.3
		$NH_4C_2H_3O_2$	2.1			$Na_2Cr_2O_7$	.3
		$NiCl_2 \cdot 6H_2O$	1.6			Stearic acid (n-heptane)	.3
		Aerosol OT (H_2O)	1.6			Stearic acid	.3
		Oleic acid (n-heptane)	1.0			$K_4Fe(CH)_6 \cdot 3H_2O$	.3
		Oleic acid	.8			$Na_4P_2O_7$(Meth Cl)	.2
		NaCl (Meth Cl)	.7			$K_3Fe(CN)_6$	.2
						$Na_2Cr_2O_7$	.2
						$Al(NO_3)_3 \cdot 9H_2O$	.1
						$Ce(NO_3)_3 \cdot 6H_2O$	.1

[a]Duplicate run.

TABLE XI. - RESULTS OF CHEMICAL ANALYSES OF SAMPLES FROM SELECTED RUNS

[Material milled, 2.5-micron nickel powder; grinding liquid, 200-proof ethyl alcohol, unless noted.]

Run	Grinding aid	Grinding time, hr	Particle size, microns	Oxygen, percent	Carbon, percent	Nitrogen, percent	Miscellaneous elements, percent
1	None (standard)	0	2.5	0.11	0.09 to 0.13	0.13	99.79 Ni; 0.008 Fe
6	CsCl	369.25	2.8	0.77	----------	----	----------
7	$BaCl_2 \cdot 2H_2O$		2.5	.82	0.41	----	0.32 Ba; <10 parts/million Cl
10	LiCl		1.8	.99	----------	----	----------
13	NaF		.8	1.25	----------	----	----------
14	$ThCl_4$		.8	4.68	----------	----	----------
16	KH_2PO_4		.5	3.54	----------	----	----------
18	$Na_4P_2O_7$		.3	2.96	0.60	----	----------
19	$K_4Fe(CN)_6 \cdot 3H_2O$		.3	2.49	----------	----	----------
20	$K_3Fe(CN)_6 \cdot 3H_3O$		.2	6.74	3.14	2.6	3.07 K
23	$Ce(NO_3)_3 \cdot 6H_2O$		.1	15.18	----------	----	----------
25	NaCl		4.1	.64	0.50	----	0.038 Na; <10 parts/million Cl
82a	$K_4Fe(CN)_6 \cdot 3H_2O$	23.75	1.6	0.66	0.36	0.10	0.13 K
82b		189.75	.3	2.35	1.06	----	----------
82c		355.75	.3	3.76	1.25	1.2	0.19 K
46	$NaCl(H_2O)$	356.75	2.3	1.15	----------	----	0.07 H_2O
47	NaCl (cyclohexane)		.7	1.52	----------	----	.0015 Na; <10 parts/million Cl
49	NaCl (Meth Cl)		.7	2.74	----------	----	----------
50	$Na_4P_2O_7(H_2O)$		1.4	1.46	----------	----	0.15 H_2O
51	$Na_4P_2O_7$ (Meth Cl)		.2	13.32	----------	----	----------

TABLE XII. - SOLUBILITY OF SALTS IN 200-PROOF ETHYL ALCOHOL AND FINAL PARTICLE SIZES OBTAINED ON GRINDING 2.5-MICRON NICKEL POWDER

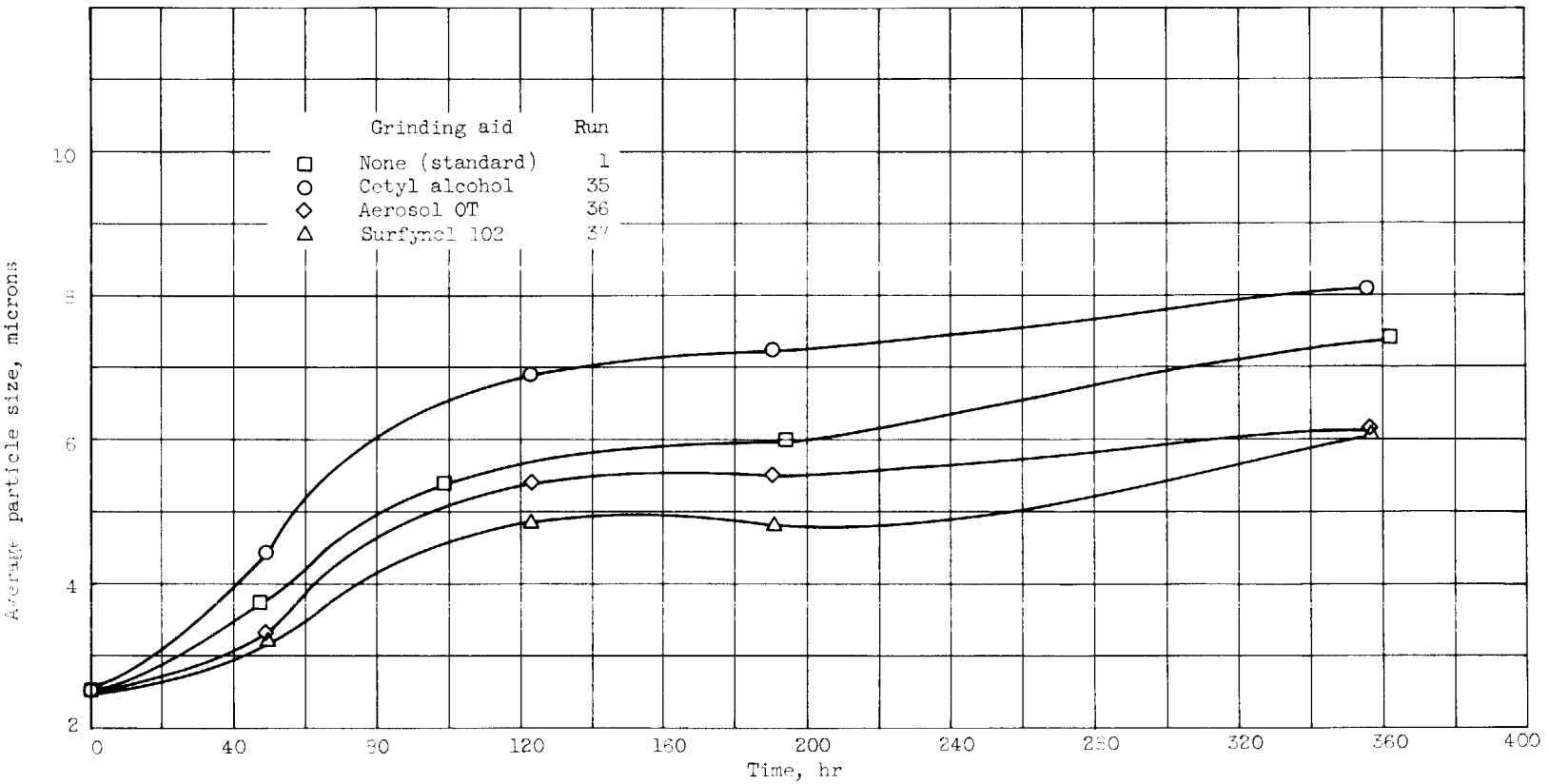
Salt (grinding aid)	Solubility, g/100 ml		Final particle size, microns
	Ref. 17	Ref. 18	
KI	14.3	1.15 at 19° C	4.9, [a]4.6
NaBr	Slightly soluble	1.83 at 20° C	4.8
NaI	Very soluble	34.9 at 30° C	4.7
NaCl	Slightly soluble	0.051 at 19° C	4.0
CsCl	Very soluble	----------	2.8
$BaCl_2 \cdot 2H_2O$	Insoluble	----------	2.6
$SnCl_4$	----------	----------	2.3
$NH_4C_2H_3O_2$	Soluble	----------	2.1, [a]2.3
LiCl	3.80 at 20° C	19.2 at 20° C	1.8, [a]2.5
$NiCl_2 \cdot 6H_2O$	Very soluble	----------	1.6, [a]1.3
$CuSO_4 \cdot 5H_2O$	Insoluble	----------	.9
NaF	Very slightly soluble	0.075 at 20° C	.8
$ThCl_4$	Soluble	----------	.8
$Al_2(SO_4)_3 \cdot 18H_2O$	Insoluble	----------	.5
KH_2PO_4	Insoluble	----------	.5
$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$	----------	----------	.4
$Na_4P_2O_7$	----------	----------	.3
$K_4Fe(CN)_6 \cdot 3H_2O$	Insoluble	----------	.3
$K_3Fe(CN)_6$	Insoluble	----------	.2
$Na_2Cr_2O_7 \cdot 2H_2O$	Insoluble	----------	.2
$Al(NO_3)_3 \cdot 9H_2O$	----------	----------	.1
$Ce(NO_3)_3 \cdot 6H_2O$	50	----------	.1

[a]Duplicate run.

TABLE XIII. - COMPARISON OF PARTICLE SIZE OF NICKEL POWDERS DETERMINED BY FISHER SUB-SIEVE SIZER AND BET METHODS

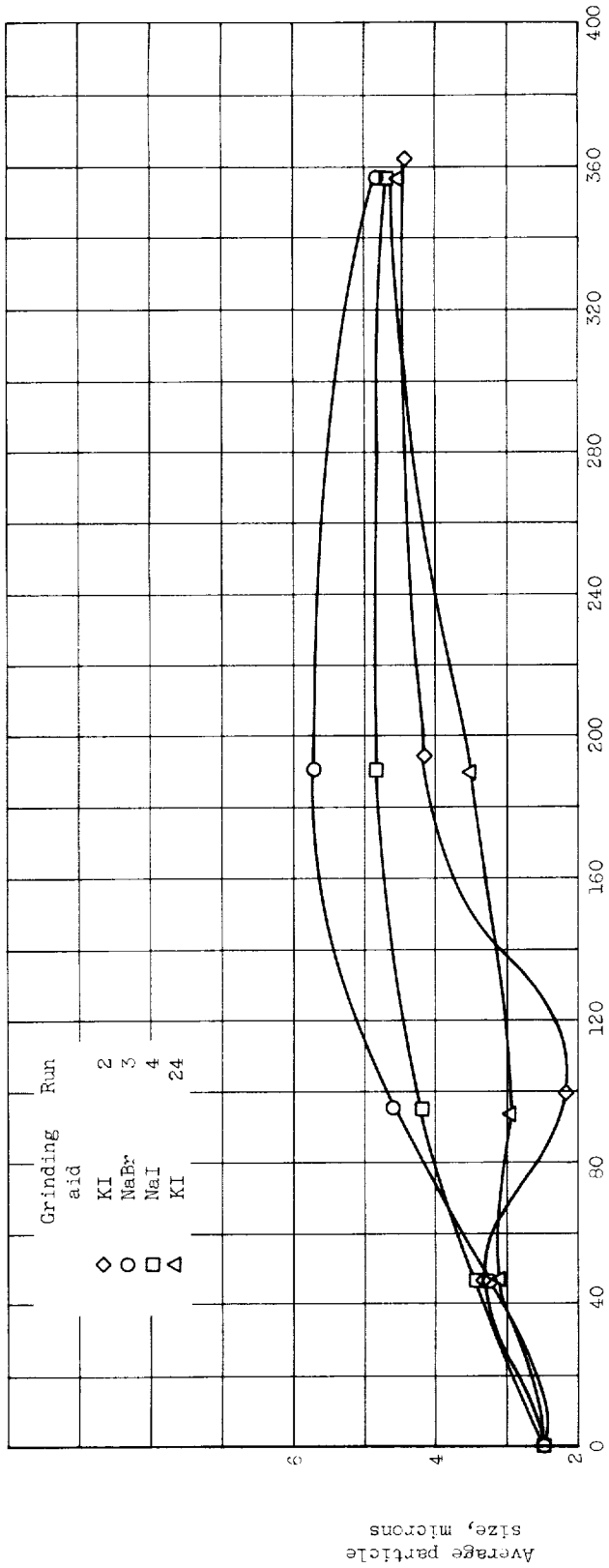
[Nickel powder milled 15 days with grinding aids in ethyl alcohol.]

Run	Grinding aid	Fisher Sub-Sieve Sizer particle size, microns	BET particle size, microns	Factor F.S.S.S./BET
--	None (as received)	2.5	2.00	1.25
15	$Al_2(SO_4)_3 \cdot 18H_2O$	0.5	0.175	2.86
16	KH_2PO_4	0.5	0.154	3.25
17	$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$	0.4	0.060	6.67
18	$Na_4P_2O_7$	0.3	0.067	4.48
19	$K_4Fe(CN)_6 \cdot 3H_2O$	0.3	0.072	4.17
20	$K_3Fe(CN)_6$	0.2	0.051	3.99
21	$Na_2Cr_2O_7 \cdot 2H_2O$	0.2	0.025	8.00
22	$Al(NO_3)_3 \cdot 9H_2O$	0.1	0.013	7.69
23	$Ce(NO_3)_3 \cdot 6H_2O$	0.1	0.011	9.09



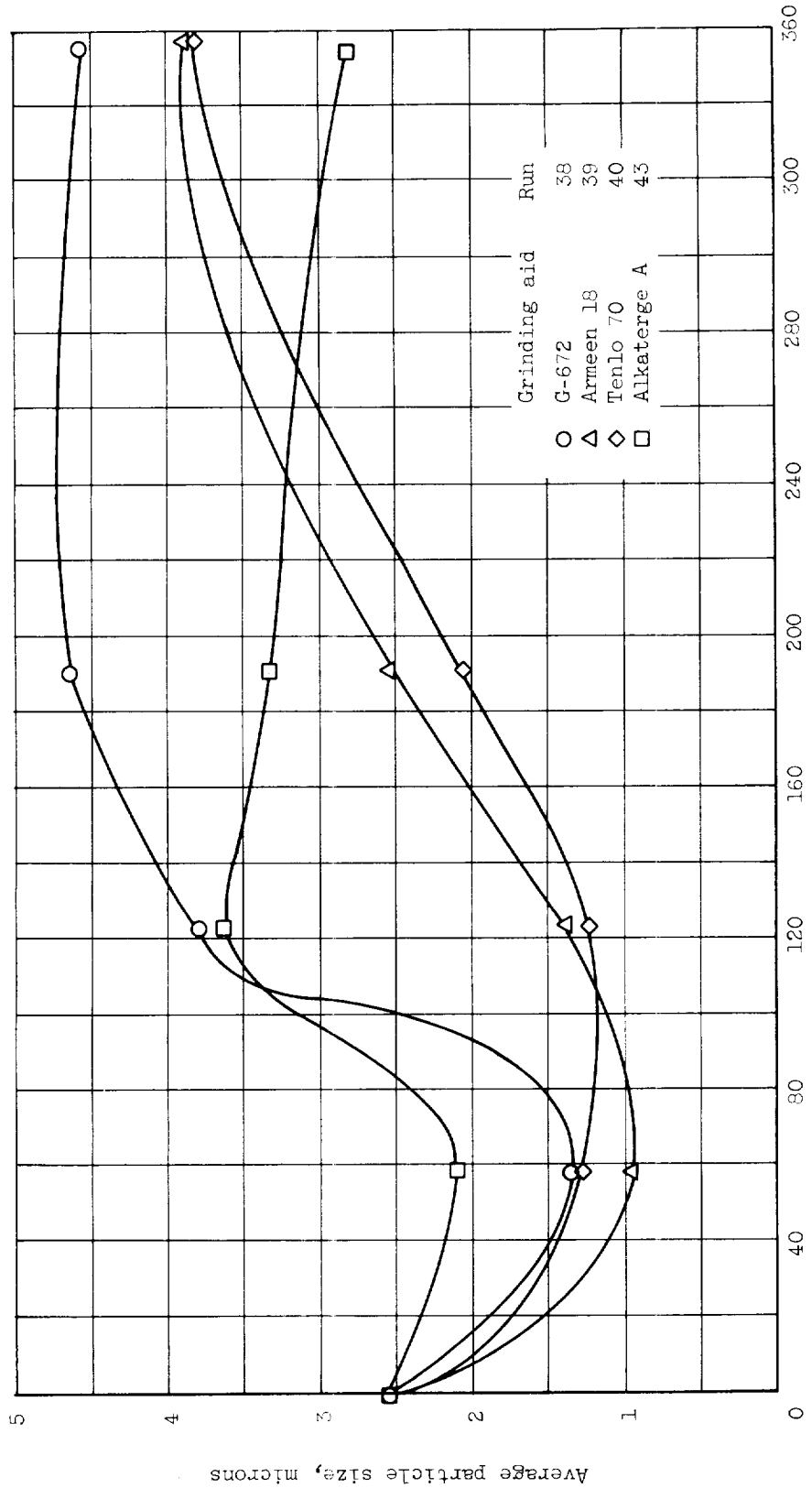
(a) Runs 1, 35, 36, and 37.

Figure 1. - Type I curves of particle size as function of grinding time. Material milled, 2.6-micron nickel powder; grinding liquid, 200-proof ethyl alcohol.



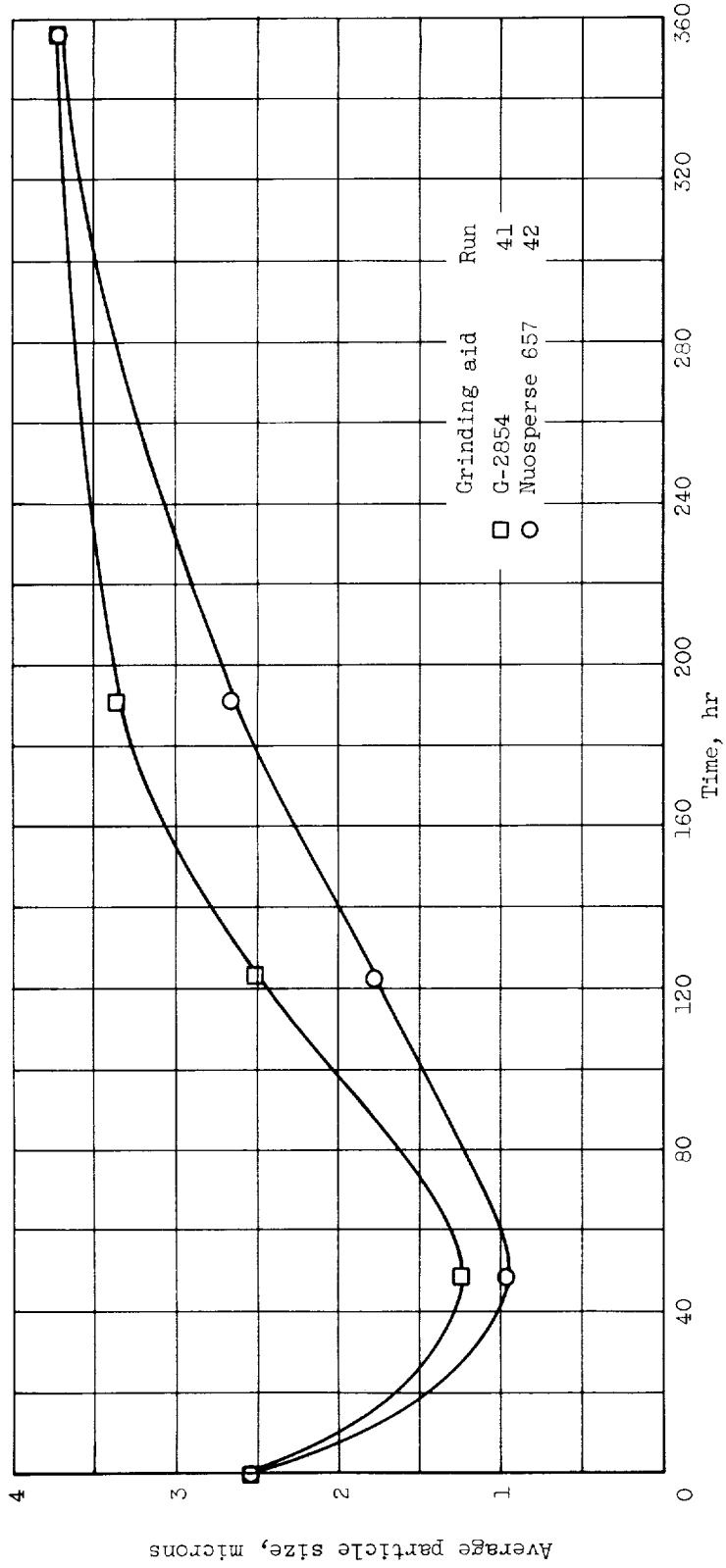
(b) Runs 2, 3, 4, and 24.

Figure 1. - Concluded. Type I curves of particle size as function of grinding time. Material milled, 2.5-micron nickel powder; grinding liquid, 200-proof ethyl alcohol.



(a) Runs 38, 39, 40, and 43. Grinding liquid, 200-proof ethyl alcohol.

Figure 2. - Type II curves of particle size as function of grinding time. Material milled, 2.5-micron nickel powder.



(b) Runs 41 and 42. Grinding liquid, 200-proof ethyl alcohol.

Figure 2. - Continued. Type II curves of particle size as function of grinding time. Material milled, 2.5-micron nickel powder.

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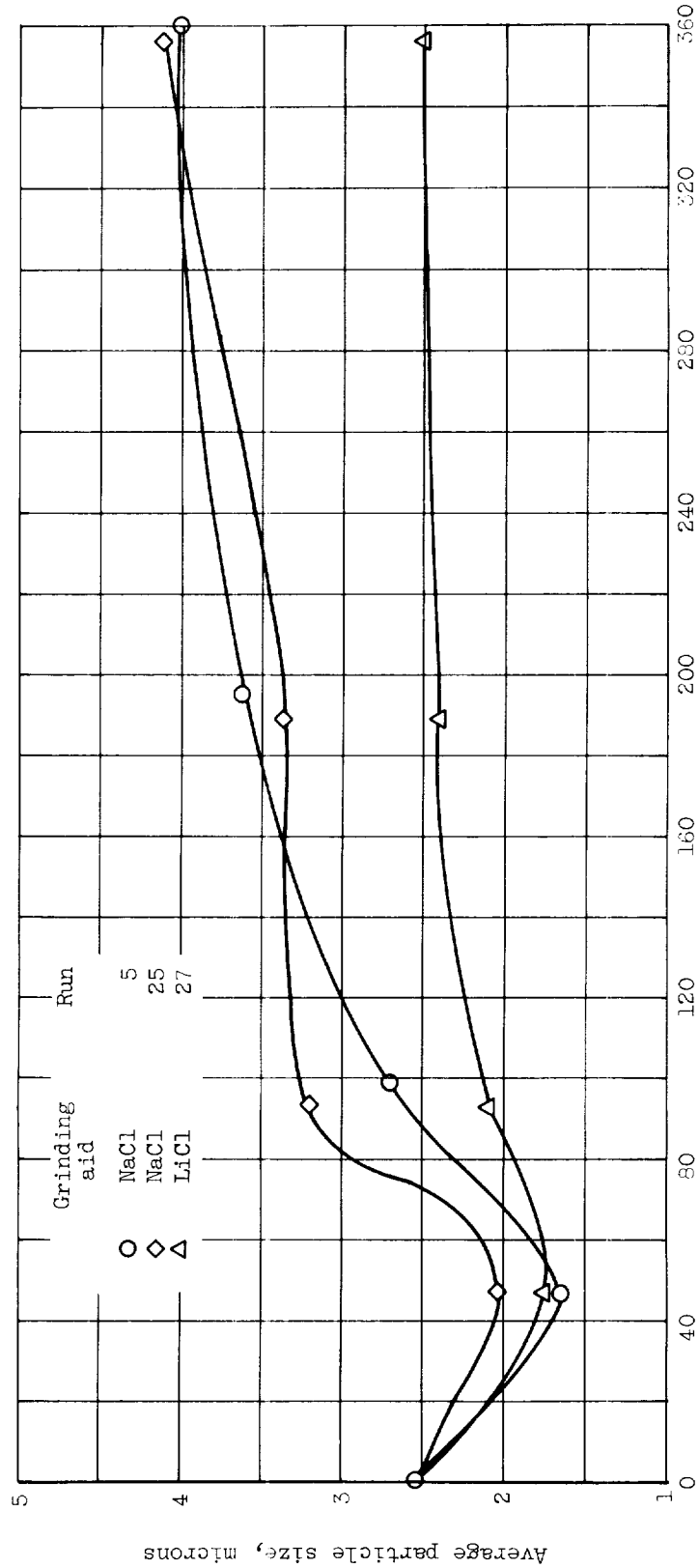
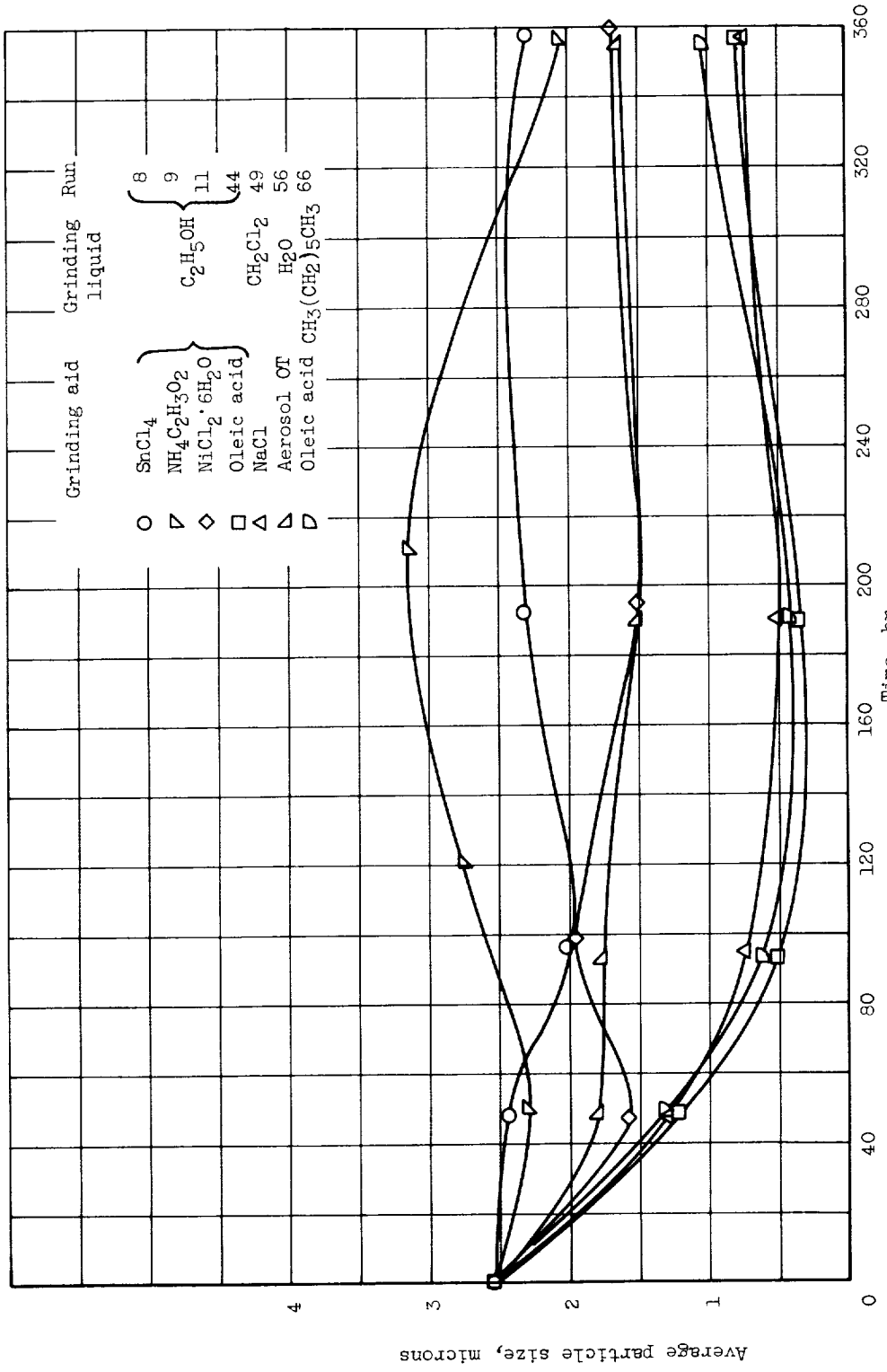


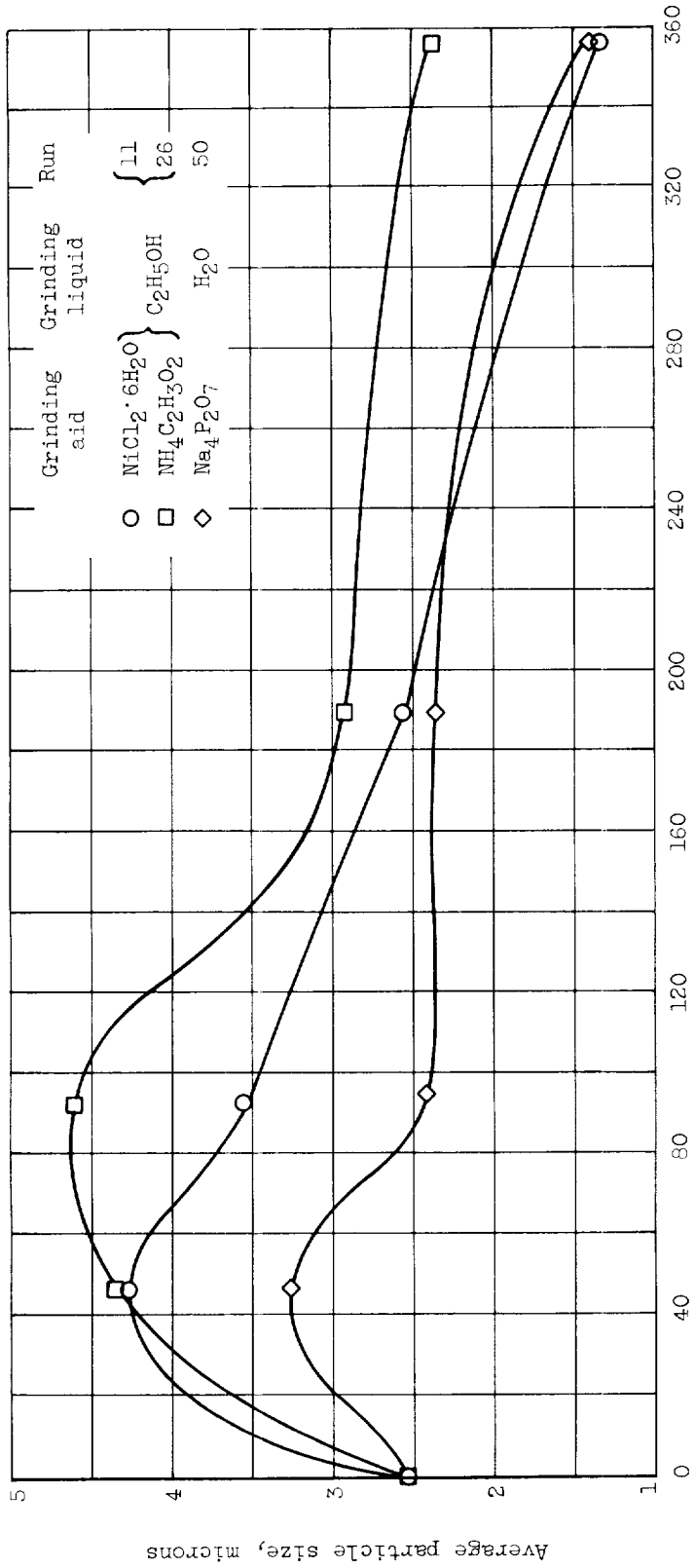
(c) Runs 5, 25, and 27. Grinding liquid, 200-proof ethyl alcohol.

Figure 2. - Continued. Type II curves of particle size as function of grinding time. Material milled, 2.5-micron nickel powder.



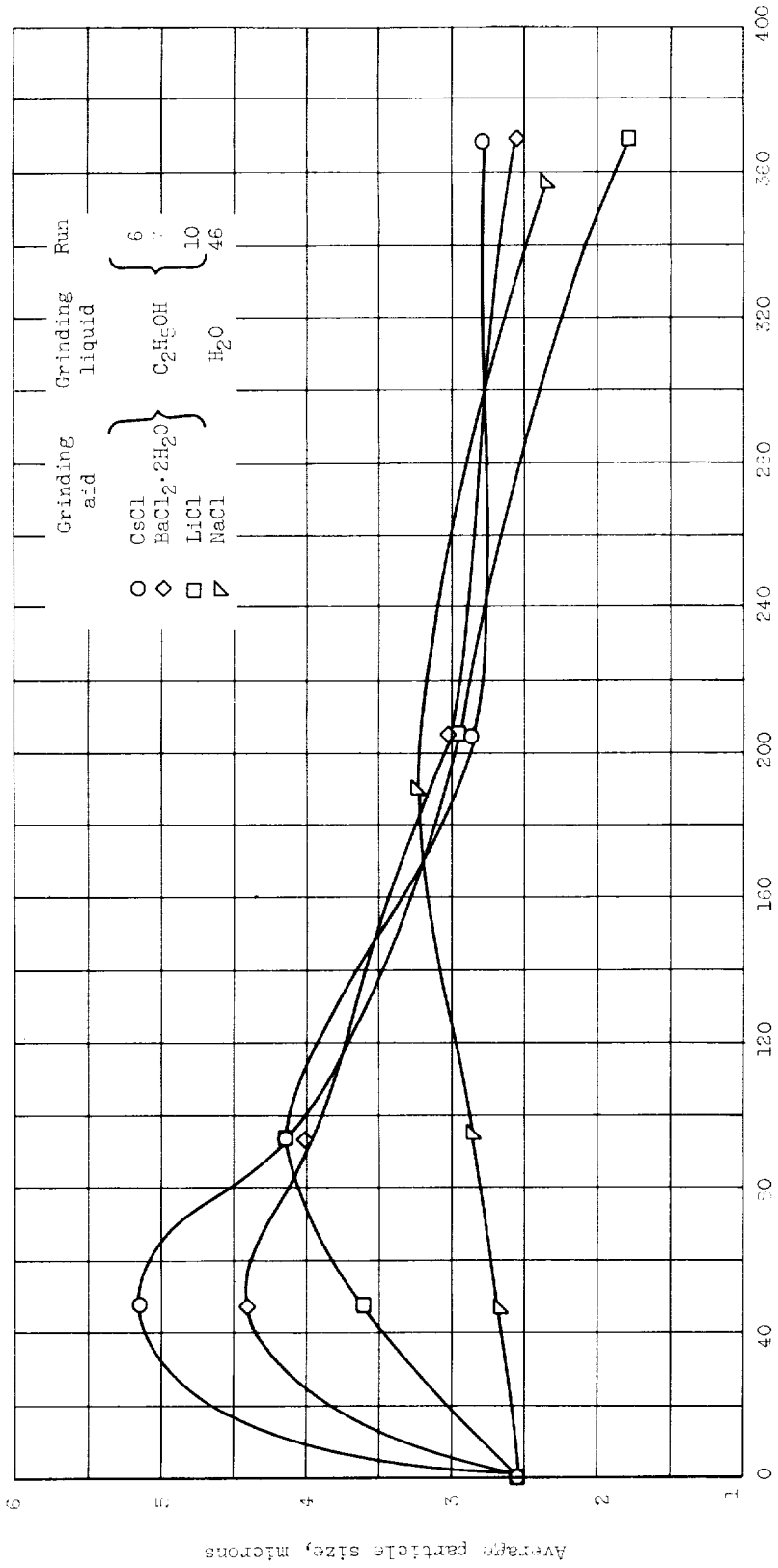
(d) Runs 8, 9, 11, 44, 49, 56, and 66.

Figure 2. - Concluded. Type II curves of particle size as function of grinding time. Material milled, 2.5-micron nickel powder.



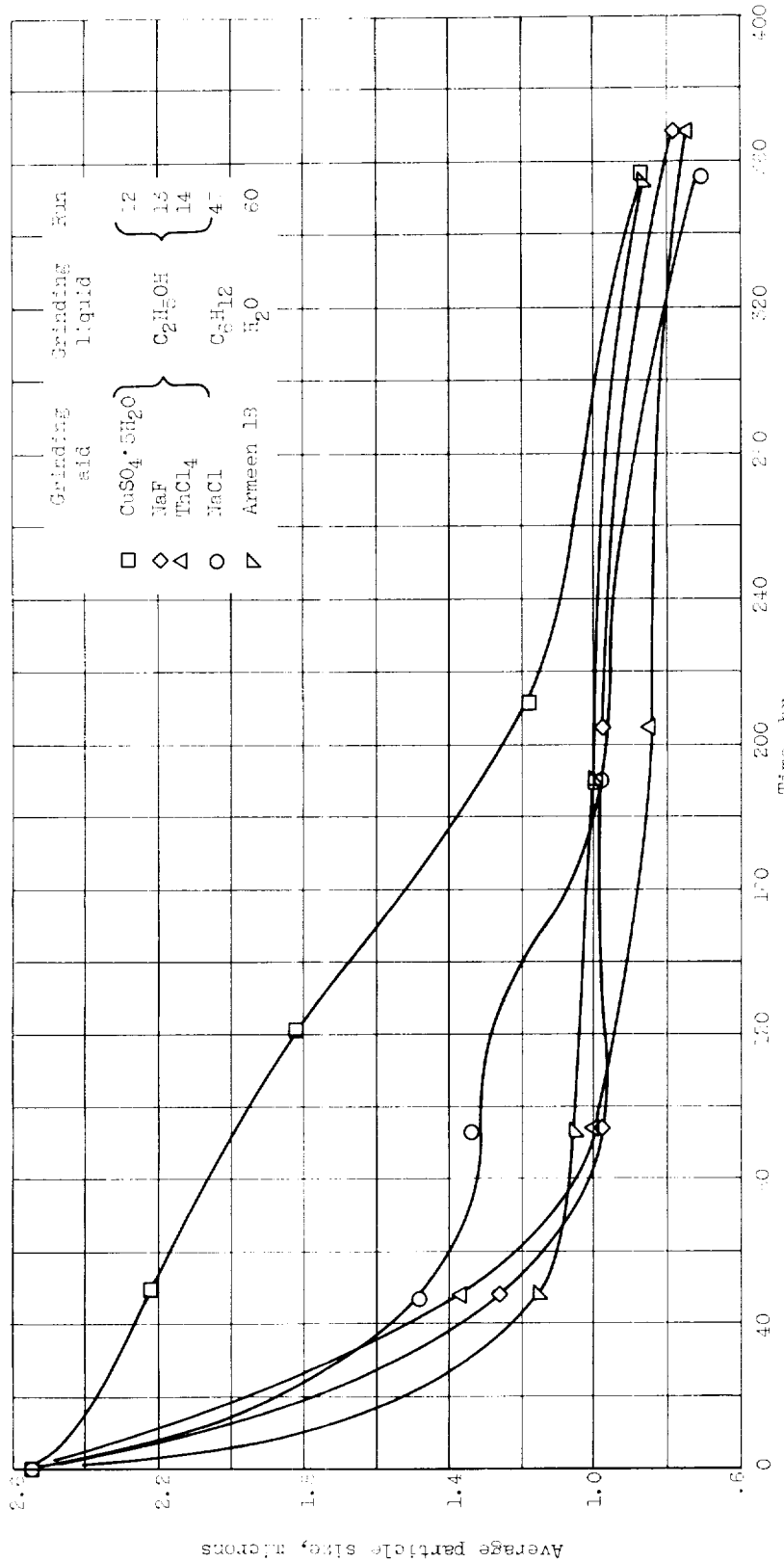
(a) Runs 11, 26, and 50.

Figure 3. - Type III curves of particle size as function of grinding time. Material milled, 2.5-micron nickel powder.



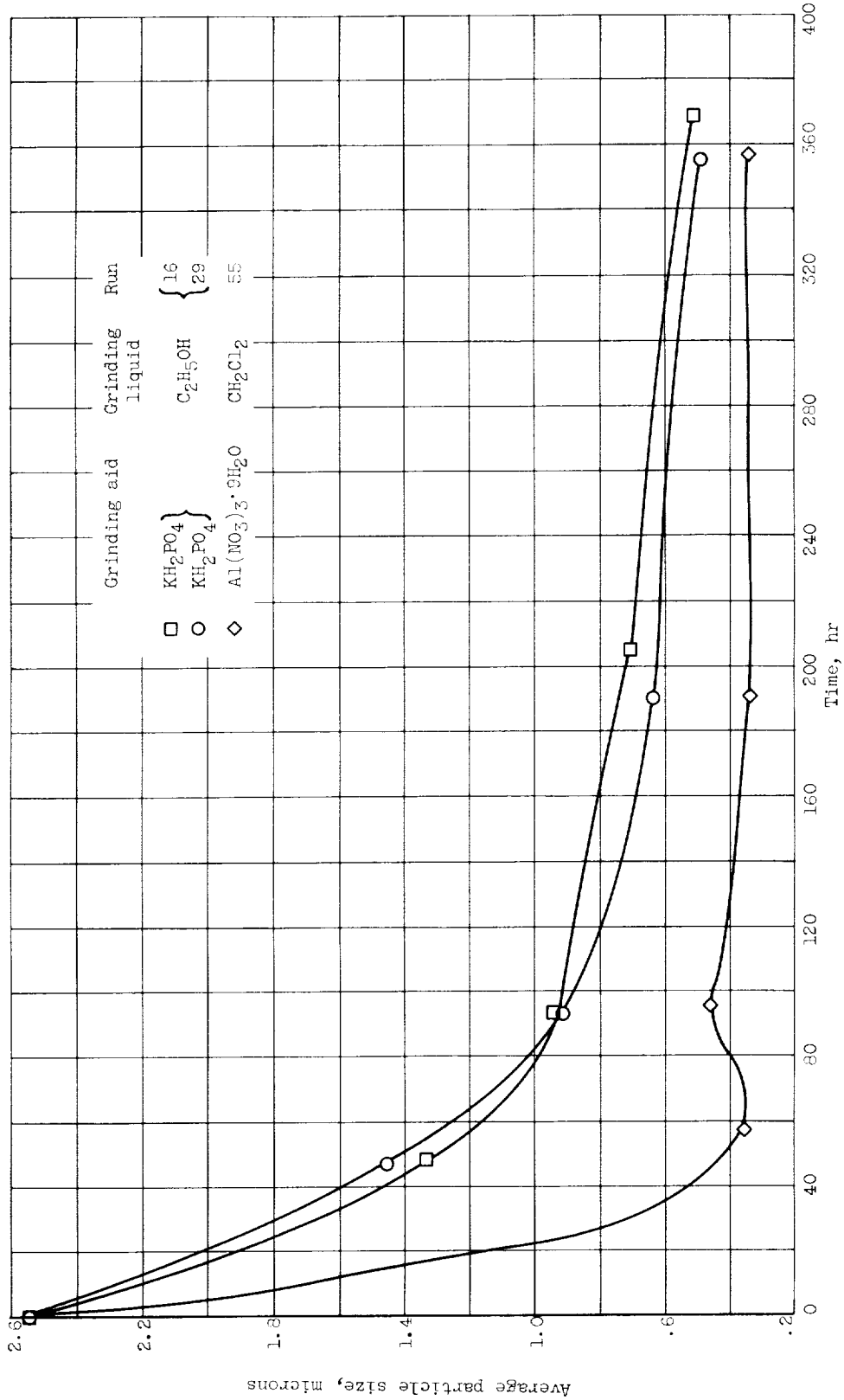
(b) Runs 6, 7, 10, and 46.

Figure 3. - Concluded. Type III curves of particle size as function of grinding time. Material milled, 2.5-micron nickel powder.



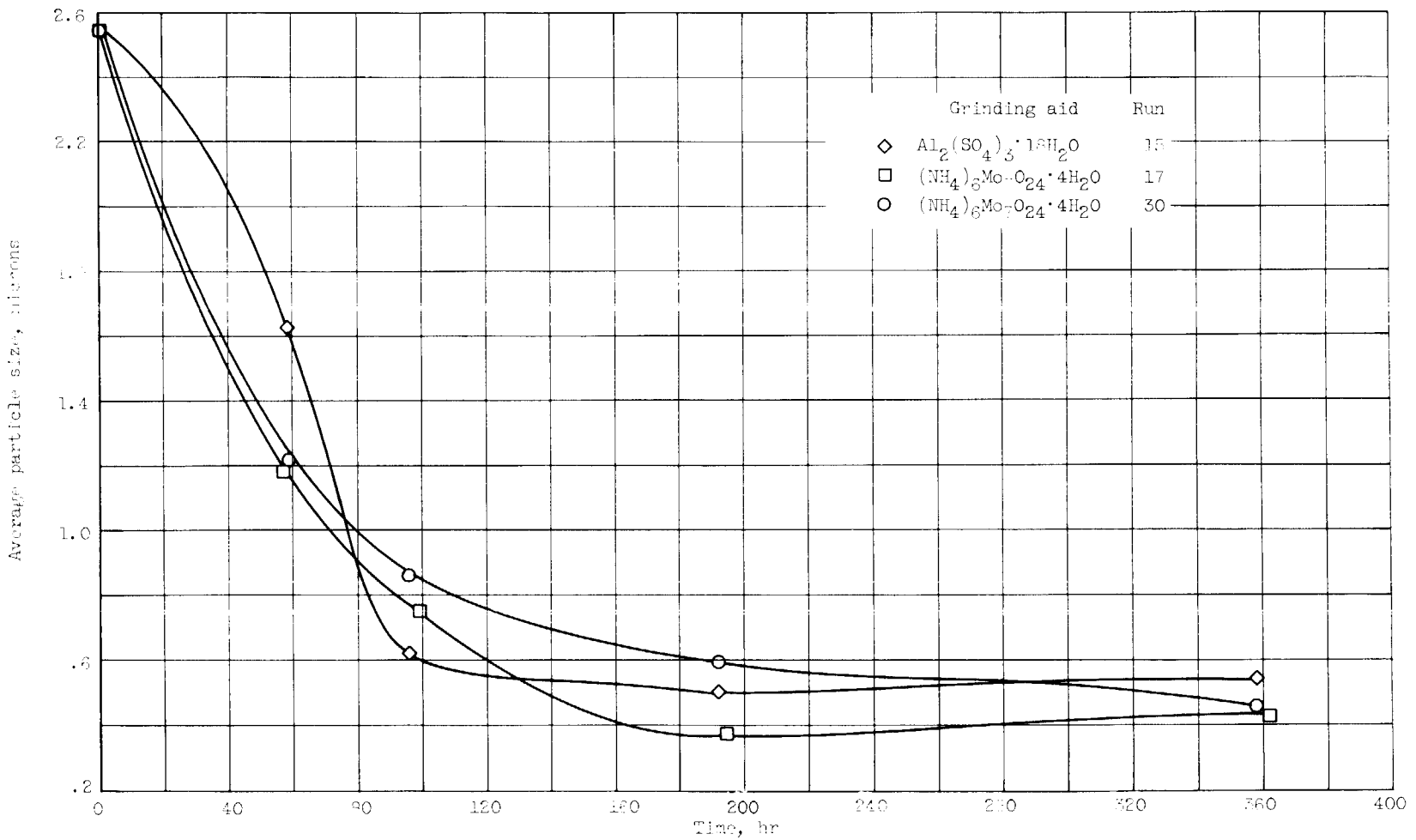
(a) Runs 12, 13, 14, 47, and 60.

Figure 4. - Type IV curves of particle size as function of grinding time. Material milled, 2.8-micron nickel powder.



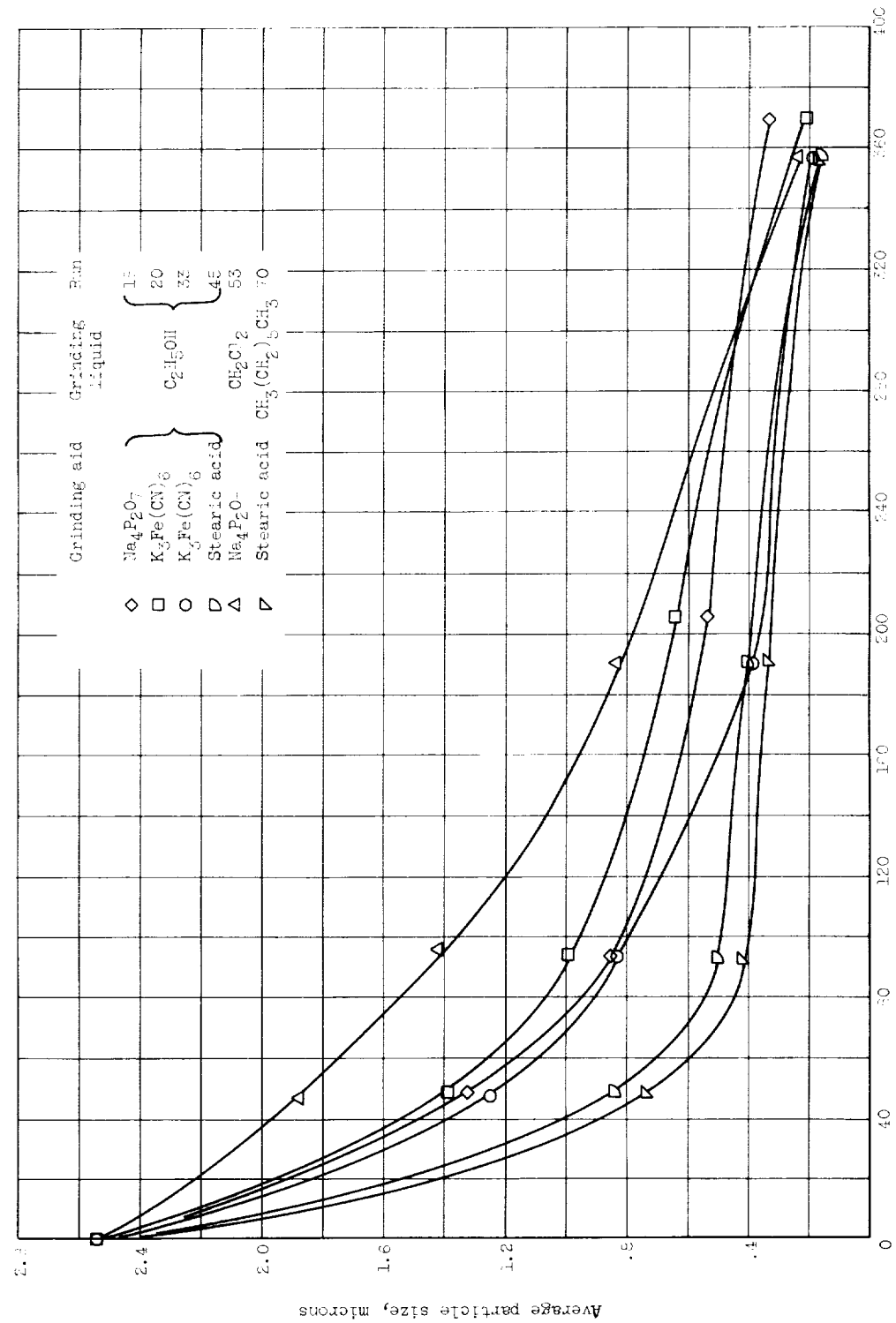
(b) Runs 16, 29, and 55.

Figure 4. - Continued. Type IV curves of particle size as function of grinding time. Material milled, 2.5-micron nickel powder.



(c) Runs 15, 17, and 30. Grinding liquid, 200-proof ethyl alcohol.

Figure 4. - Continued. Type IV curves of particle size as function of grinding time. Material milled, 2.5-micron nickel powder.



(d) Runs 15, 20, 22, 45, 53, and 70.

Figure 4. - Continued. Type IV curves of particle size as function of grinding time. Material milled, 2.5-micron nickel powder.

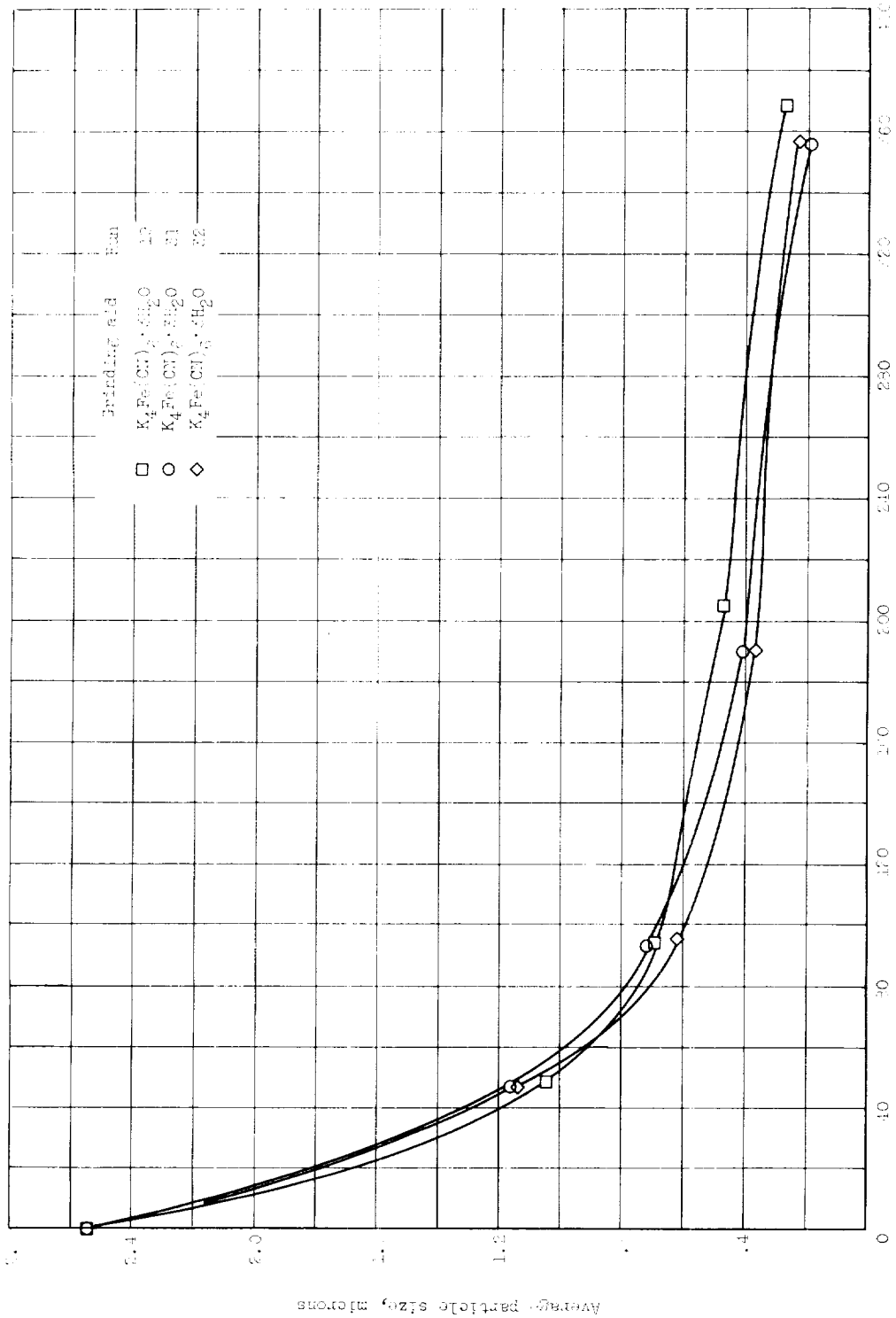
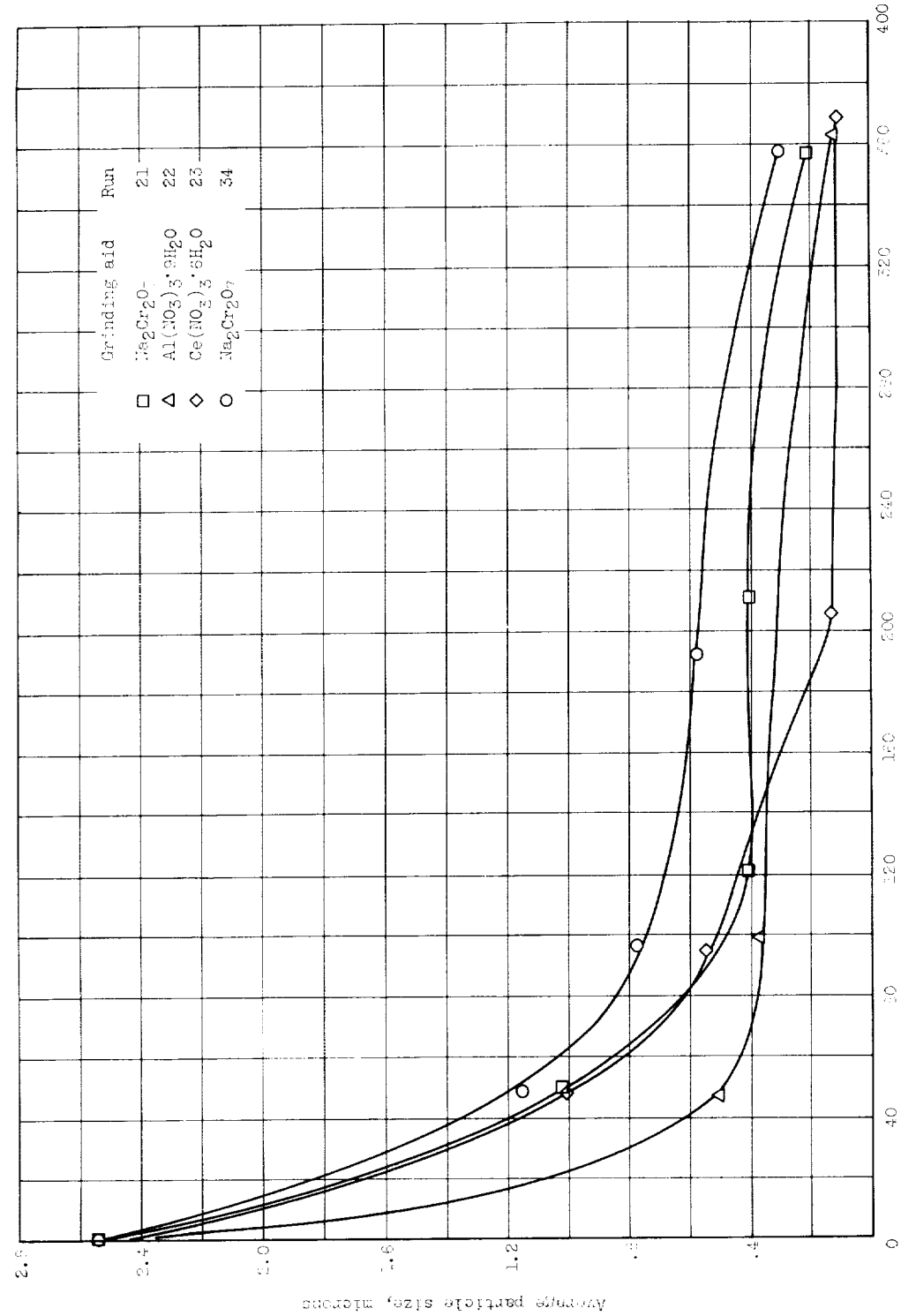


Figure 4. - Continued. Type 17 curves of particle size as function of grinding time. Material milled, 2.5-micron nickel powder.



(c) Runs 21, 22, 23, and 34. Grinding liquid, 200-proof ethyl alcohol.

Figure 4. - Concluded. Type IV curves of particle size as function of grinding time. Material milled, 2.5-micron alox powder.

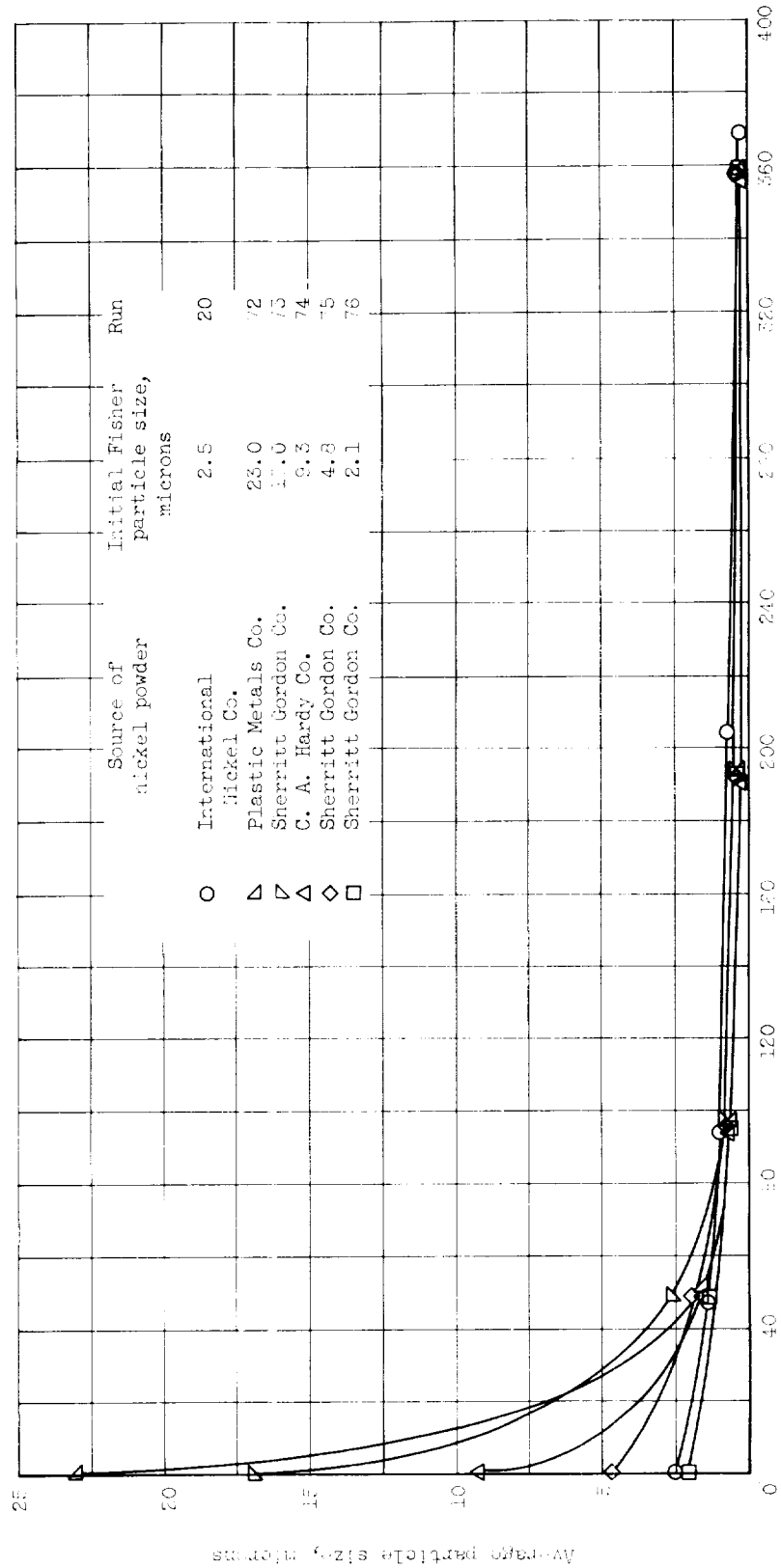
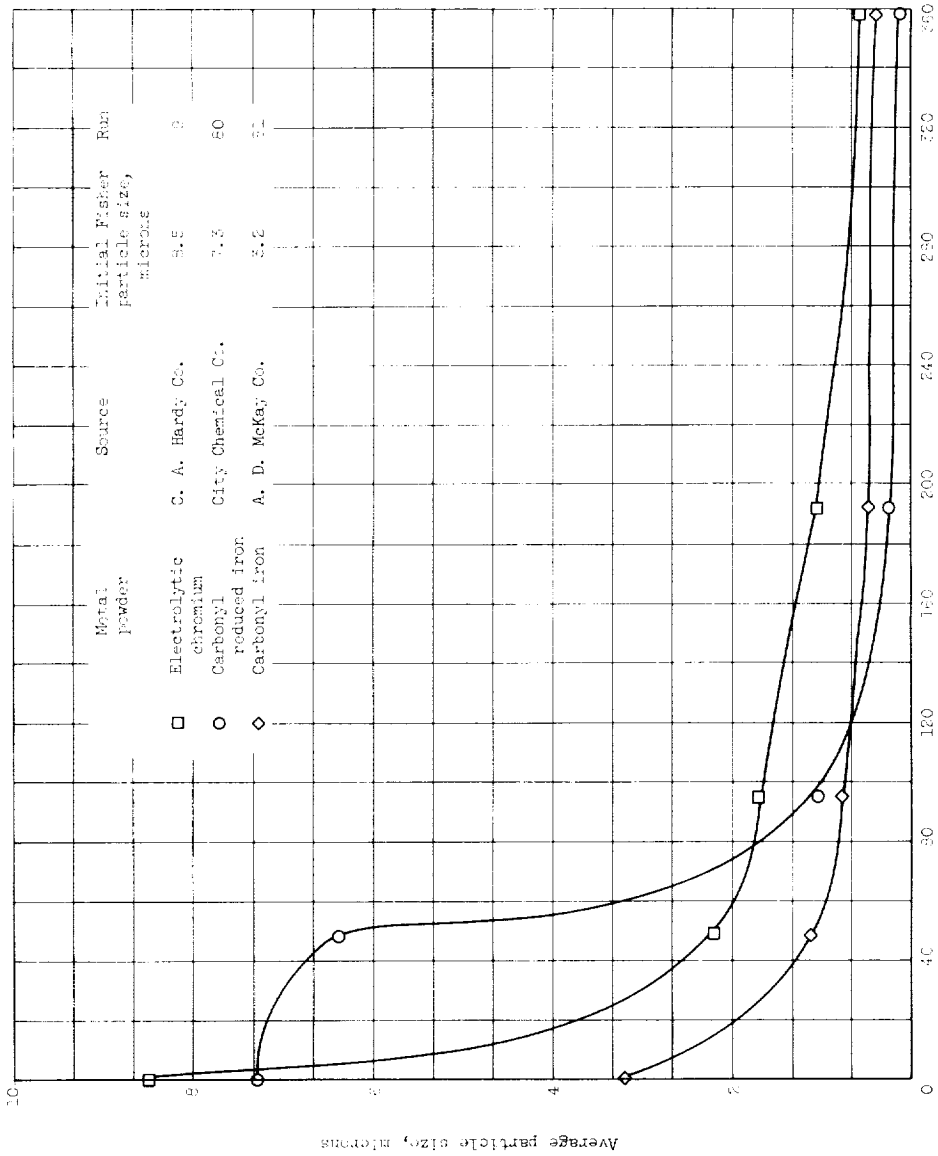


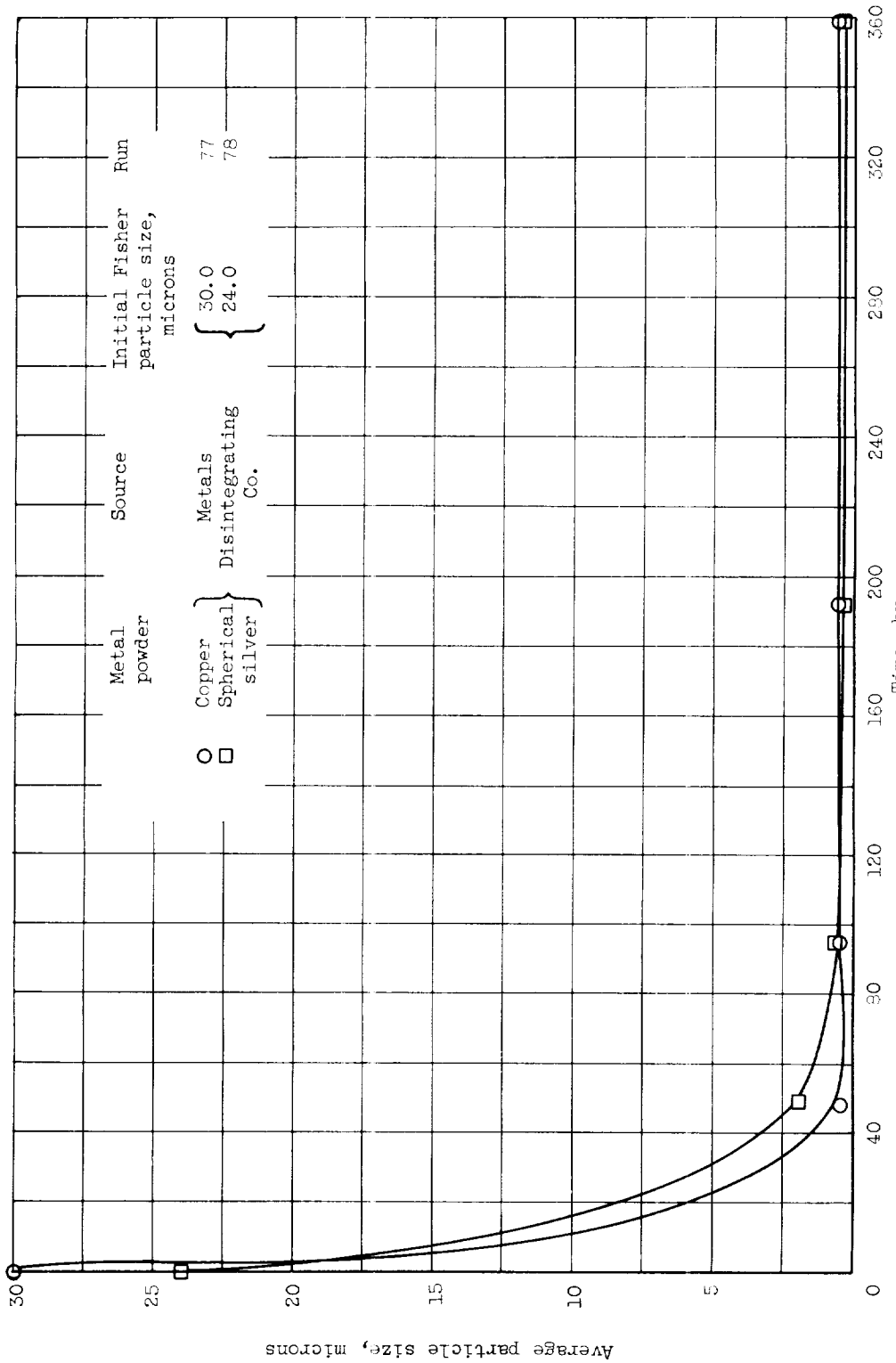
Figure 1. - Type IV curves of particle size as function of grinding time for various metal powders. Grinding liquid, 200-proof ethyl alcohol; grinding aid, potassium ferricyanide.

(a) Nickel powder.



(c) Chromium and iron powder.

Figure 5. - Concluded. Type IV curves of particle size as function of grinding time for various metal powders. Grinding liquid, 200-proof ethyl alcohol; grinding aid, potassium ferricyanide.



(c) Copper and silver powder.

Figure 5. - Concluded. Type IV curves of particle size as function of grinding time for various metal powders. Grinding liquid, 200-proof ethyl alcohol; grinding aid, potassium ferricyanide.

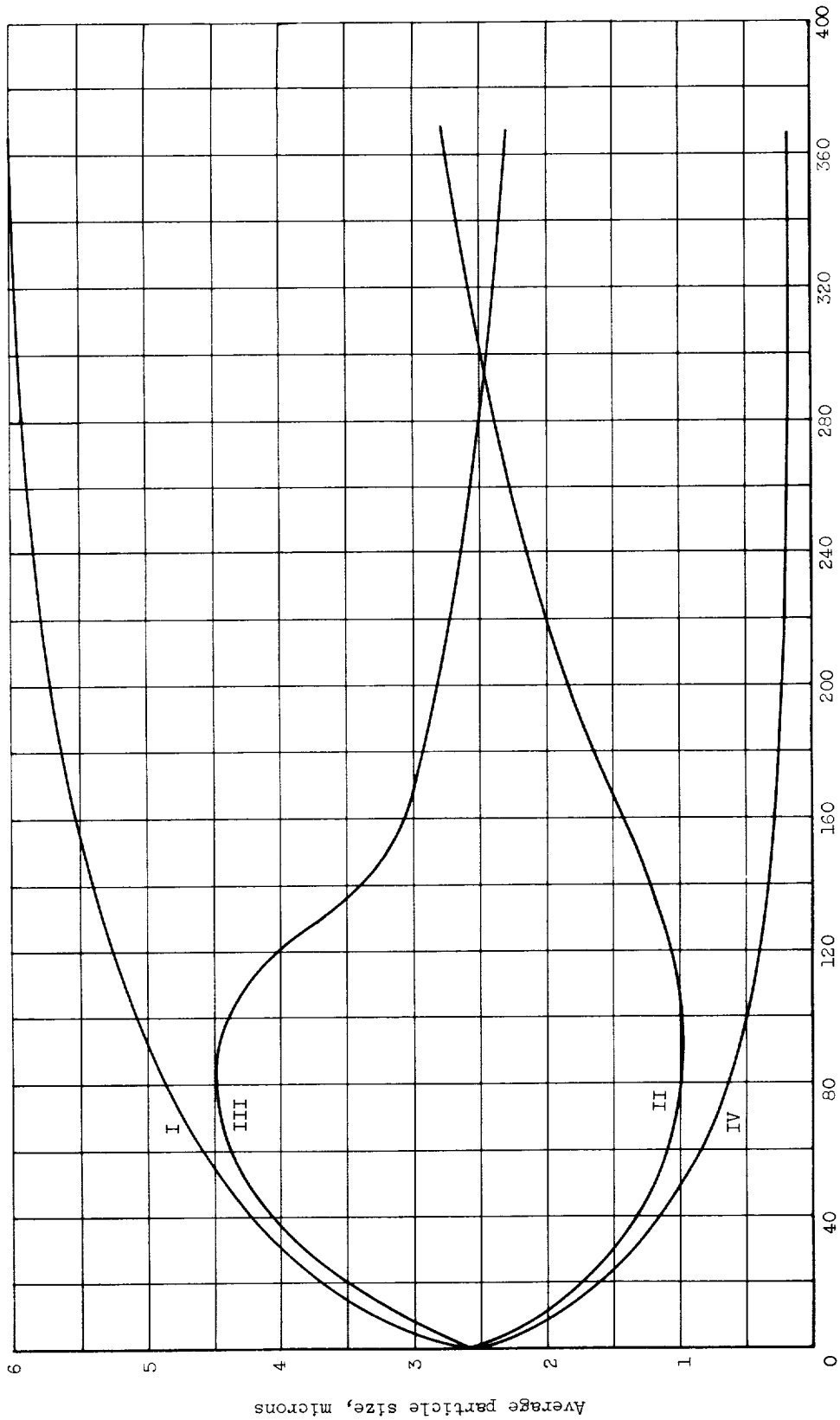


Figure 6. - Generalized curves of types I to IV.

Run	Ion	Ion size, A (a)	Particle size, microns
15	Al	0.50	0.5
22	Al	.50	.1
10	Li	.60	1.8
11	Ni	.70	1.6
8	Sn	.71	2.3
3	Na	.95	4.8
4	Na	.95	4.7
5	Na	.95	4.0
13	Na	.95	0.8
18	Na	.95	.3
21	Na	.95	..2
12	Cu	.96	.9
23	Ce	1.01	.1
2	K	1.33	4.9
19	K	1.33	.3
20	K	1.33	.2
7	Ba	1.35	2.6
6	Cs	1.69	2.8

[a]Ref. 19.

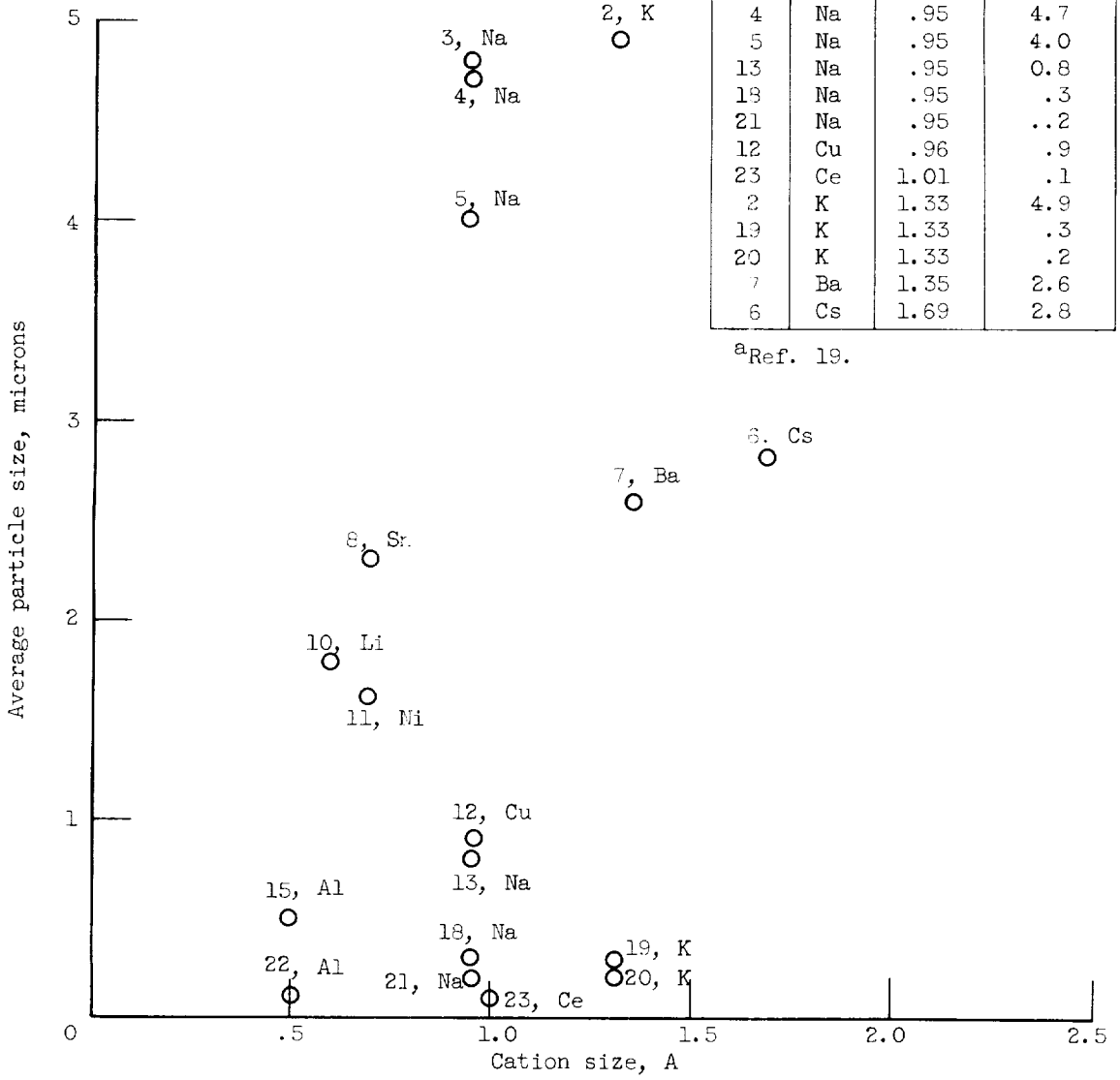


Figure 7. - Particle size as function of size of salt cation. Material milled, 2.5-micron nickel powder; grinding liquid, 200-proof ethyl alcohol; data from table IV.

Run	Ion	Ion size, A (a)	Particle size, microns
13	F	1.36	0.8
5	Cl	1.81	4.0
6	Cl	1.81	2.8
7	Cl	1.81	2.6
8	Cl	1.81	2.3
10	Cl	1.81	1.8
11	Cl	1.81	1.6
14	Cl	1.81	0.8
3	Br	1.95	4.8
2	I	2.16	4.9
4	I	2.16	4.7

[a]Ref. 19.

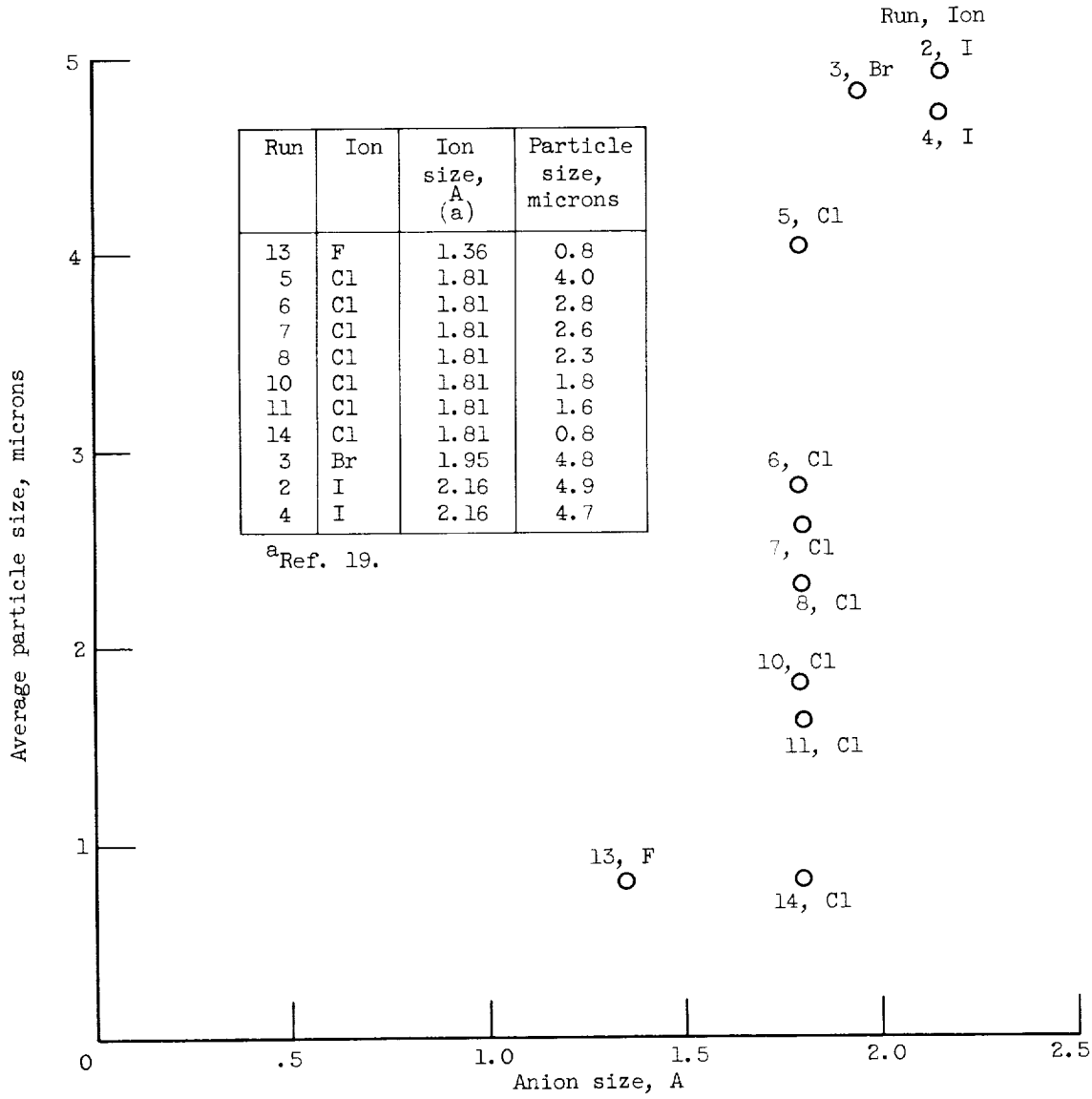
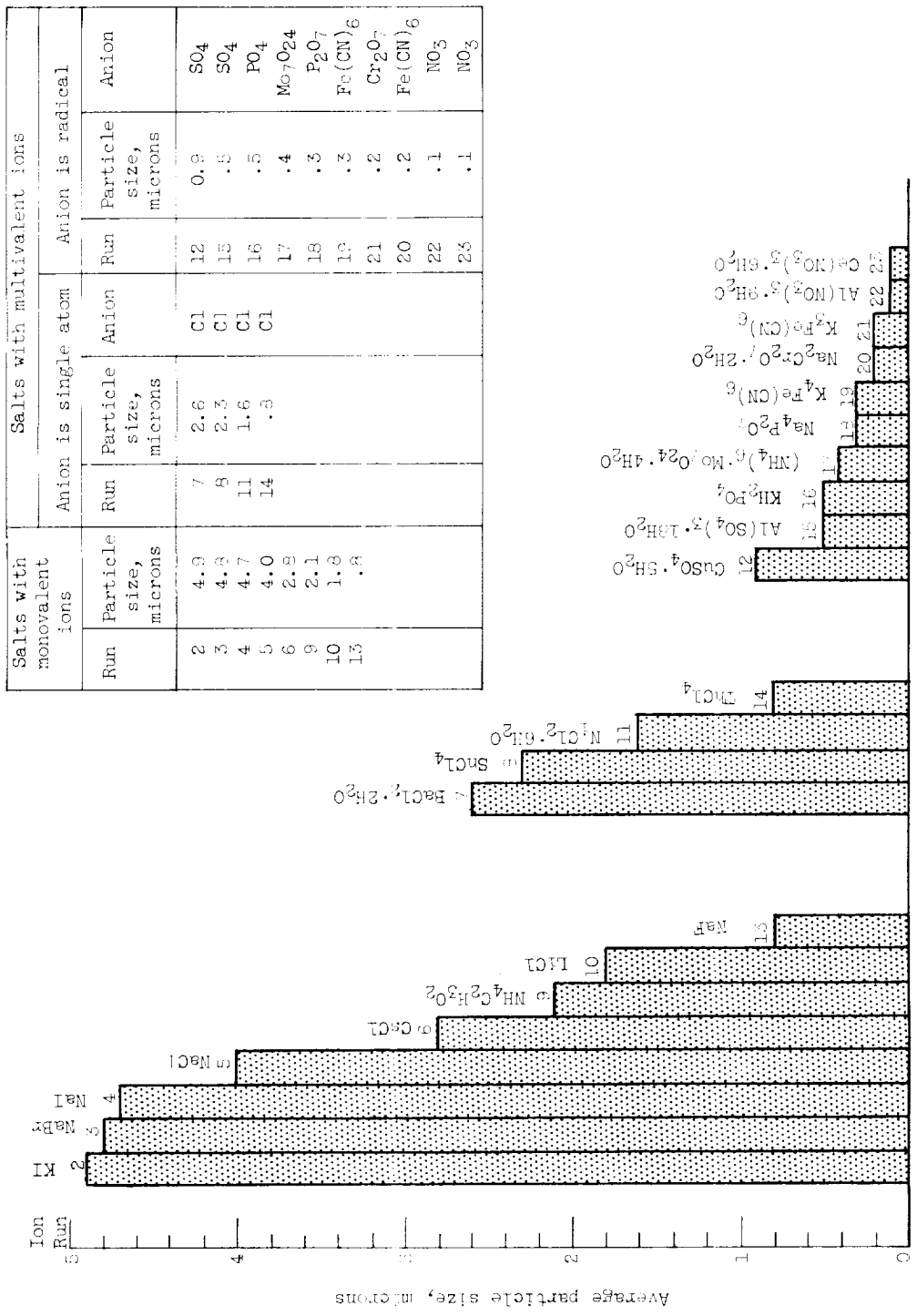


Figure 8. - Particle size as function of size of salt anion. Material milled, 2.5-micron nickel powder; grinding liquid, 200-proof ethyl alcohol; data from table IV.



Salts with monovalent ions		Salts with multivalent ions							
		Anion is single atom				Anion is radical			
Run	Particle size, microns	Run	Particle size, microns	Anion	Run	Particle size, microns	Anion
2	4.9	7	2.6	Cl	12	0.3	SO_4
3	4.3	8	2.3	Cl	15	.5	SO_4
4	4.7	11	1.6	Cl	16	.5	PO_4
5	4.0	14	.3	Cl	17	.4	Mo_7O_{24}
6	2.9				18	.3	P_2O_7
9	2.1				19	.3	$Fe(CN)_6$
10	1.3				21	.2	Cr_2O_7
13	.8				20	.2	$Fe(CN)_6$
					22	.1	NO_3
					23	.1	NO_3

Figure 3. - Particle size as function of valence and complexity of salt ions. Material milled, 2.5-micron nickel powder; grinding liquid, 200-proof ethyl alcohol; data from table IV.